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13. ABSTRACT (Maximum 200 words) AIM: To develop economical low-temperature routes to biomimetic synthesis of high-performance composite materials, with control of composition and structure based on the molecular mechanisms controlling biomineralization of calcium- and silicon-based nanocomposites. HIGHLIGHTS: We report success in our originally proposed transition from analysis of biological systems to the development of useful applications across a broad range of materials. We discovered that the silicateins - proteins we originally discovered responsible for the structure-directing catalysis of polymerization to form silica and silsesquioxanes - also can be used for the structure-directing polymerization of titanium dioxide from the appropriate water-stable alkoxide precursor. This result dramatically extends our initial development of the new field we called "Silicon Biotechnology" to an even broader "Functional Inorganic Materials Biotechnology." We also demonstrated this year that the self-assembling diblock copolypeptides that we developed as biomimetic analogs of the silicateins can be used to direct the nanofabrication of potentially valuable core-shell fluorescent quantum dots and narrow line-width microlasers. SIGNIFICANCE: These results demonstrate that we can use biotechnology to resolve the mechanisms used by nature to make high-performance composites, and successfully apply the information to develop new routes to synthesis of novel composites with exceptional control of composition and nanostructure.				
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**NEW HYBRID ROUTE TO BIOMIMETIC SYNTHESIS**

**FINAL REPORT**

March 21, 2003

U.S. ARMY RESEARCH OFFICE

DAAH04-96-1-0443

UNIVERSITY OF CALIFORNIA  
SANTA BARBARA

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## SUMMARY OF RESEARCH HIGHLIGHTS

The basic premise underlying our MURI project in Biomimetic Synthesis is that analysis and creative adaptation of the mechanisms used to control mineral-organic composite synthesis in living systems can lead to the development of novel routes to the economical synthesis of high-performance hybrid materials uniquely suited to advanced applications of interest to the Army. Anticipated advantages for materials synthesis include new insights into the mechanisms used by biology to control nanofabrication and hierarchical synthesis with structural precision exceeding the capabilities of present human engineering; more intimate coupling at the organic-inorganic interface in hybrid materials; and novel routes to synthesis and structural control of high-performance composites, over multiple, hierarchically controlled length-scales, under environmentally benign conditions. Focusing on a few carefully selected model systems of biomineralization with silicon and calcium, and using a highly integrated interdisciplinary approach that unites the skills and approaches of researchers in 6 different departments and two colleges, our work in this second year of our MURI program has begun to deliver on its initial promise: We have discovered previously unanticipated mechanisms controlling the nanofabrication of mineralized composites in living systems, and have applied these basic insights in our development of novel routes for the synthesis of high-performance mineral-organic composites, including oriented mesoporous and macroporous materials with a wide range of functionalities and unique properties, with structural control extending over nanoscale, mesoscale and macroscale dimensions. Advanced applications of several of the resulting new materials are under development. Highlights are summarized below.

Support for this effort from the ARO has catalyzed augmentation from the University, the State of California, the UCSB Materials Research Laboratory (a national MRSEC), private industries (with which we collaborate closely) and other federal agencies. The diversity and broad base of this synergistic support, and the strength of the commitment it represents, are indicated in the list included at the beginning of this report (see Synergistic Funding). The development and use of advanced instrumentation unique to this project and to UCSB is a vital part of our effort, as described below. Integration of these developments with cutting-edge biotechnology, materials chemistry, chemical engineering and processing is fairly unique to our program. We have fused our research groups to more efficiently apply the tools and approaches of these disciplines in concert to a shared objective; as a result, you will notice that many of our research personnel are cross-listed between two or three labs and departments. Students and postdoctorals in this program thus receive an unusually strong cross-disciplinary training: Materials scientists, chemical engineers, physicists and chemists work closely on a daily basis with one another and with biotechnologists, molecular and cell biologists. They are finding excellent opportunities for subsequent employment or further training as a result (see Scientific Personnel, below).

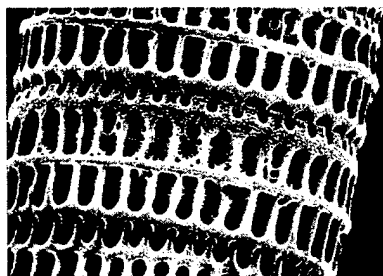
### Highlights:

We are pleased to report success in our initially proposed transition from the analysis of biological systems to the development of useful applications across a broad range of materials. We discovered that the silicateins - proteins we originally discovered responsible for the structure-directing catalysis of polymerization to form silica and silsesquioxanes - also can be

used for the structure-directing polymerization of titanium dioxide from the appropriate water-stable alkoxide precursor. This result dramatically extends our initial development of the new field we called "Silicon Biotechnology" to an even broader "Functional Inorganic Materials Biotechnology." We also demonstrated that the self-assembling diblock copolypeptides that we developed as biomimetic analogs of the silicateins can be used to direct the nanofabrication of potentially valuable core-shell fluorescent quantum dots and narrow line-width microlasers. We discovered the mechanism of synthesis of the natural micro/laminate armor of the abalone shell, and we discovered a new class of self-healing polymers that combine the strength of kevlar with the toughness of silicones.

#### **Background: Enabling Discoveries by the Applicant Team:**

Biology accomplishes the synthesis of nanostructured materials and components with a precision of 3-dimensional nanoscale architectural control that far exceeds the capabilities of present human technology. Furthermore, biological nanofabrications occur at relatively low temperatures, ambient pressure, at near-neutral pH and in the absence of caustic chemicals, in marked contrast to present human manufacturing technologies (Morse, 2000, 2001).



Nanoscale features in the silica wall of the marine diatom, *Diploneis*. (Length 50  $\mu\text{m}$ .)

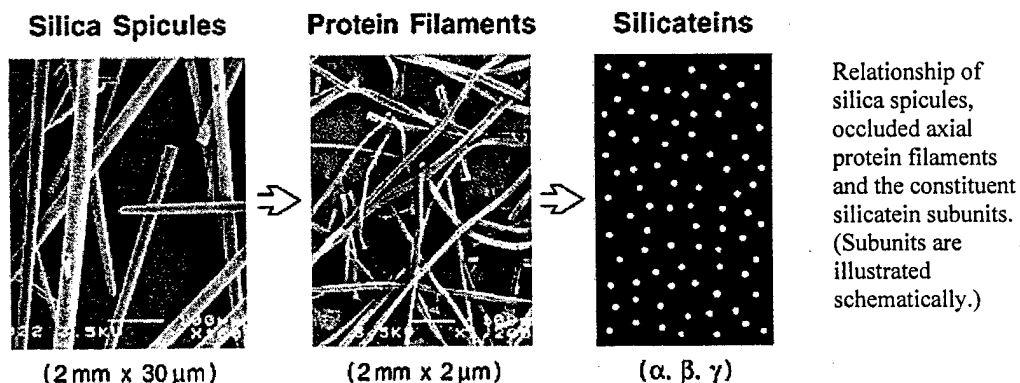
We proposed for our MURI research that the analysis and harnessing of the underlying biological mechanisms governing such precision nanofabrication will offer a broad spectrum of economically practical and environmentally benign novel routes to manufacturing of high-performance nanocomposites and nanostructured optoelectronic, photonic, electronic and magnetic materials with increased precision of structural control that should directly translate to increased performance of the resulting materials and devices. We anticipated applications in improved microelectronic and optoelectronic devices (for switching, communications and sensors); and durable composites for construction, fabrication, separation media, selective barrier layers, catalysts, photovoltaics, etc. We are pleased to report here that we have begun to deliver on this promise. As evidence of the industrial significance of the "silicon biotechnology" we developed (Morse, 1999), we note that Dow Corning and Genencor, Inc. (two industrial sponsors of our past research) have recently announced a \$38-million investment and strategic alliance to pursue objectives in this area (Potera, 2001).

We discovered that the silica made by a marine sponge provides a uniquely tractable model system for dissection of the molecular mechanisms controlling siloxane nanofabrication, and that the integral proteins of these and other biomineralized composites can be used to direct the formation of thin films of silica and other minerals with useful optical, electrical and magnetic properties (Shimizu et al., 1998; Cha et al., 1999, 2000a, 2000b; Zhou et al., 1999; Morse, 1999, 2000, 2001; Stevens et al., 2000; Shimizu and Morse, 2000; Belcher et al., 1998 & in prep.). These findings are extensions of our earlier discovery that the proteins that control mineral nucleation and determine crystal polymorph selection and atomic lattice orientation during nanofabrication of the abalone shell and abalone pearl can be used to direct the synthesis

of multiphasic microlaminate composite materials, over mesoscopic dimensions, with precise fidelity corresponding to their control *in vivo* (Fritz et al., 1994; Belcher et al., 1996, 1998). Most significantly, we discovered that the proteins we purified from the biosilica catalyze the polymerization of silica, and serve as a template directing its deposition! This represents the first discovery of a protein from a biosilica that directly controls silica polymerization (although this activity has been sought for more than a century; cf. Bendz and Lindqvist, 1977; Simpson and Volcani, 1981). This also represents the first discovery of an enzyme that catalyzes formation of an inorganic material in biology.

Many sponges contain large quantities of fine needles (spicules) or larger structural elements made of silica (fiberglass) containing inner cores and/or surrounding sheaths of protein. The potential value of these materials as optical fibers has been demonstrated (Cattaneo-Vietti et al., 1996). The integral proteins had long been suspected to control the synthesis, structures and properties of silica nanocomposites made by sponges (Simpson and Volcani, 1981; Simpson, 1984; Simkiss and Wilbur, 1989), but how they might act as templates, envelopes or modifiers of silica polymerization and nanofabrication of the composite remained unknown (Simpson, 1989). Similarly, the possible role of intracellular occlusions of silicates found in some sponges (Harrison, et al., 1974; Imsiecke and Müller, 1995) remains unclear. Hecky et al. (1973) suggested that the hydroxyl side chains of proteins might serve as templates to align silicic acid monomers prior to condensation and polymerization in diatom wall formation, and Kröger et al. (1996) had isolated a family of hydroxyl-rich proteins from the envelopes surrounding these walls. Hildebrand, Volcani and their colleagues (1997, 1998) cloned and characterized a silicon-specific family of membrane-transporters from diatoms. But the molecular mechanisms of silica-composite formation and its control had remained unclear until quite recently.

We found that the silica spicules made by the common California shallow-water sponge, *Tethya aurantia* provide an ideal model system for studies of biosilicate nanofabrication and its control. This sponge, readily collected near Santa Barbara, yields ca. 60% of its dry weight as silica spicules (ca. 2 mm x 30 micron diam.). To our surprise, we found that the integral protein structure is quite simple. A central filament of protein can be purified from these spicules by dissolution of the surrounding silica with buffered hydrofluoric acid (HF), permitting easy purification of the integral proteins in large quantities. These protein filaments consist of regular, repeating (X-ray diffracting) subassemblies of three very similar subunits, that we named silicateins (for silica proteins), present in the approximate ratio 12:6:1 ( $a_{12}b_6g_1$ )<sub>n</sub> (Shimizu et al., 1998; Cha et al., 1999). The filaments can be readily depolymerized and the constituent protein subunits purified by gel electrophoresis.



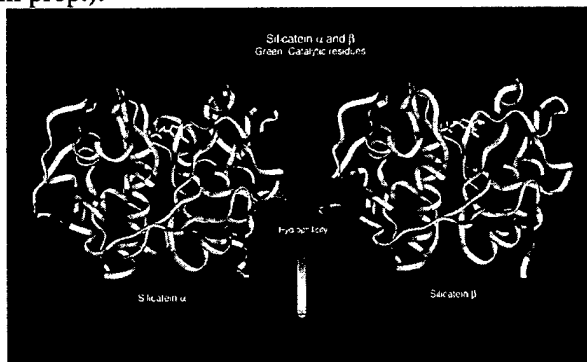
Peptide sequencing, cDNA cloning, and sequence analyses of the cloned cDNAs that code for these proteins revealed the surprising fact that the silicateins are highly homologous to cathepsin L, a member of the well-known super-family of papain-like proteolytic (protein hydrolyzing) enzymes (Shimizu et al., 1998; Cao and Morse, in prep.). The silicateins and protease exhibit a striking 77% overall sequence homology (52% identity, and an additional 25% close similarity, when the sequences are aligned and compared point-for-point). This discovery led to the recognition that the silicateins and the proteases (hydrolases) must have evolved from a shared molecular ancestor (Shimizu et al., 1998; Zhou et al., 1999; Morse, 1999, 2000, 2001; Shimizu and Morse, 2000). Most significantly, we discovered, the catalytic "active site" of the protease (hydrolase) is preserved with only minor changes in the silicateins.

The surprising discovery that the proteins occluded within a biologically formed silica structure are closely similar to a well known family of enzyme catalysts, led us to predict (Shimizu et al., 1998) and then experimentally confirm (Cha et al., 1999; Zhou et al., 1999; Morse, 1999, 2000, 2001) that the silicateins are in fact active as catalysts, capable of catalyzing the polymerization of silica. Furthermore, we discovered, these proteins act not only as catalysts (catalyzing the hydrolysis and subsequent condensation of silicon alkoxide monomers at neutral pH, in a reaction that otherwise requires extremes of pH and heat; cf. Cha et al., 1999), but also exhibit a "scaffolding" or structure-directing template-like activity, in which they direct the assembly of the polymerized silica to follow the molecular counters of the underlying protein filament. **This discovery thus explained for the first time how proteins can accomplish the control of silicon polymerization, while simultaneously directing the nanostructural architecture of the silica that is formed, all at low temperature and neutral pH (in contrast to present industrial conditions of manufacture, that require harsh acid or alkali for catalysis, and frequently require high temperatures as well).** [Recently, Kröger et al. (1999) in Germany have used a similar approach to discover a family of proteins occluded within the silica of diatoms that also catalyze silica polymerization, although these proteins do not apparently act as structure-directing templates.] We discovered that the silicatein proteins also exhibit these two activities with organically substituted silicon alkoxides, catalyzing and spatially directing the polymerization of phenyl- and methyl- silsesquioxanes to make structure-directed **silicones** at neutral pH (Cha et al., 1999)! The catalytic activity is abolished by thermal denaturation, proving that it depends on the intact 3-dimensional conformation of the silicatein proteins.

#### **Identification, Characterization and Biomimetic Duplication of the Determinants Responsible for Catalytic Activity:**

We found that this catalytic activity also is present in the disaggregated silicatein subunit monomers, and - most significantly - in the purified and reconstituted silicatein a and b subunits produced by bacteria from cloned, recombinant DNAs (Cha et al., 1999, Zhou et al., 1999; Morse, 1999, 2000, 2001; Cao and Morse, in prep.). This later evidence proves that the silicatein subunit alone is sufficient for catalysis of siloxane polymerization from the silicon alkoxide precursor, with no other component required. Because the silicateins are highly homologous to cathepsin L - and this homology includes the exact conservation and position of 6 cysteine (-SH sidechain) residues that form three intramolecular disulfide crosslinks in the proteases - we can be confident that the homology between the proteins includes the major features of their 3-dimensional conformations. Since the structure of the protease is known from X-ray

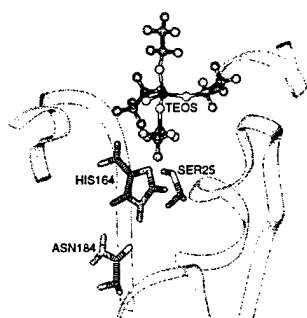
crystallography to the 1.78 Å level of resolution, further energy-minimization corrections to reflect the unique sequences of the silicateins thus provide us with good three-dimensional molecular models of these silica-synthesizing proteins (Shimizu and Morse, 2000; Cao and Morse, in prep.).



Molecular models of silicatein  $\alpha$  and  $\beta$ . The two structures are quite similar. Both show the active site cleft between the alpha-helix- and beta-sheet-dominated halves of the molecule. The active site serine and histidine residues are shown in stick figures spanning the top of the cleft.

Because we found that the structure of the known catalytic active site of the protease is conserved with high fidelity in the silicateins, and because the molecular mechanism of catalysis of the proteases is known in very precise detail, we were able to make very specific predictions concerning the detailed molecular mechanism of silicatein catalysis of the rate-limiting step in silicon-oxygen polymerization from the alkoxide substrates at neutral pH (Cha et al., 1999, Zhou et al., 1999; Morse, 1999, 2000, 2001).

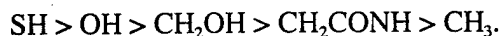
Taking advantage of our ability to express the catalytically active silicateins from recombinant DNA templates cloned in bacteria, we then tested and confirmed these predictions by site-directed mutagenesis, a genetic engineering method enabling us to replace at will any amino acid in the silicatein protein (Zhou et al., 1999; Morse, 1999, 2000, 2001; Cao and Morse, in prep.). Using this approach, we replaced each of the two specific amino acid residues (histidine and serine) projecting into the active-site cleft whose side-chains we predicted to be essential for catalysis in the silicatein molecule with a non-functional methyl group, in both the silicatein a and b subunits. As predicted, both of these replacements significantly inactivated the silicatein, confirming our hypothesis of its mechanism of catalysis. In further confirmation of this mechanism, we recently have demonstrated that the activity of the histidine-deficient mutant can be "rescued" or complemented by exogenous imidazole, whereas the serine-deficient mutant cannot be restored by exogenous imidazole (Merget and Morse, in prep.). Other site-directed mutagenesis studies confirm the predicted ancillary role of the asparagine residue, the third predicted and highly conserved member of the "catalytic triad" of residues at the catalytic active site of the silicateins (Cao and Morse, in prep.)



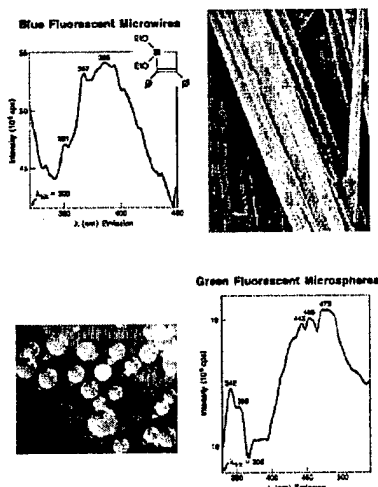
Detailed structure of the active site of Silicatein  $\alpha$  combining with a siloxane substrate (TEOS). Details were deduced from our site-directed mutagenesis (genetic engineering) studies elucidating the roles of the three residues illustrated in the mechanism of catalysis, in conjunction with 3D molecular modeling.



We then further confirmed the reaction mechanism that we had proposed, and demonstrated that we could harness this mechanism, by designing wholly synthetic peptides that mimic the activity of the silicateins (Cha et al., 2000a, 2000b). We synthesized a family of self-assembling diblock copolypeptides incorporating the features that we found (from the cDNA analyses, site-directed mutagenesis) and molecular modeling to be essential for catalysis by the silicatein active site. Like the silicateins on which they are based, these relatively simple synthetic peptides prove capable both of catalyzing the polymerization of silicon alkoxides at neutral pH and directing the structure of the resulting silica (Cha et al., 2000a). Systematic variation of the residues used in the synthesis of these biomimetic diblock copolypeptides confirmed the identification (based on the molecular modeling and site-directed mutagenesis studies cited above) of the requirement for a specific nucleophilic residue and a hydrogen-bonding amine, and extended these conclusions by demonstrating that the rate and extent of silica polymerization catalysis is proportional to the strength of the nucleophile, over the following homologous series:



When the most effective of these biomimetic, self-assembling diblock copolypeptides is used as the structure-directing catalyst of silica polymerization, and the product doped by incorporation of the fluorescent silicon alkoxide substrate-analog, 1,1-dibutoxy, 2,3 diphenyl, 5-isopentenyl-silacylcobutene, further evidence of the structure-directing activity of these catalysts is observed (see figure below).



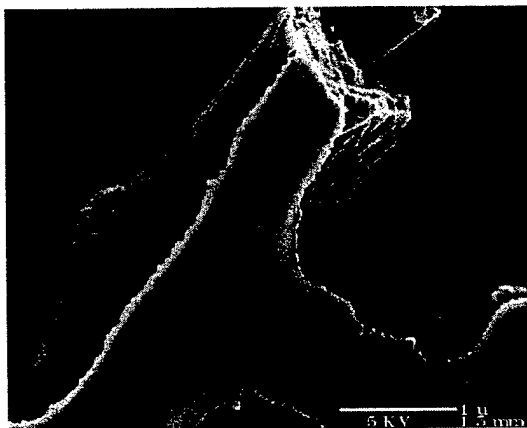
Incorporation of the fluorogenic substrate analog, silacylcobutene alkoxide, in silica formed by the silicatein-biomimetic, self-assembling peptide that acts as a structure-directing catalyst of polymerization (cf. Cha et al, 2000a). Emission spectra and micrographs show that the same peptide catalyst produces either blue fluorescent microwires or green fluorescent microspheres, depending on its molecular topology and hierarchical organization.

When concatenated in a supramolecular chain, the peptide serves as a template for the synthesis of long fibrillar bundles of silica and fluorescent polysiloxane (upper figures). When concatenation is prevented, the individual peptide molecules direct the synthesis of fluorescent glassy spheres (lower figures).

### Recent Breakthrough: Control of $\text{TiO}_2$ Synthesis and Structure:

We recently discovered that the silicatein biocatalyst also catalyzes and structurally directs the polycondensation of  $\text{TiO}_2$  network materials at neutral pH and low temperature, starting from the appropriate alkoxide-like precursors! This exciting discovery (Sumerel and Morse, in 2003) demonstrates that we can extend the range of the work described above to other metallo-oxanes, and that what we first saw as the dawn of "silicon biotechnology" (Morse,

1999, 2000, 2001; Shimizu and Morse, 2001) is in fact the opening of an approach to much broader "inorganic materials biotechnology."



TiO<sub>2</sub> growth on silicatein. Note that growth of the metal oxide occurs on the surface of the underlying silicatein filaments. These protein filaments serve both as the polycondensation-promoting catalyst and structure-directing template.

We have found that the key to the structure-directing activity of the silicateins and their biomimetics appears to reside in the fact that they are relatively slow catalysts; the slow rate of catalysis apparently permits relatively weak interactions on the protein or peptide surface to serve as templates, guiding the alignment and polycondensation process to follow the molecular contours of the polymer (see figure above). Whereas most of the conventionally used silicon alkoxides (such as, for example, titanium isopropoxide) are unstable in water and hydrolyzed and condensed spontaneously, obscuring any effect the silicatein might have on the reaction and the structure of the product (Morse et al., unpublished observations), the bidentate alkoxides of simple polyols and carbohydrates are water stable, and these serve as suitable substrates for structure-directed polycondensation catalyzed by silicatein. Thus, the bis-lactato complex of titanium is an appropriately useful precursor for structure-directed synthesis of TiO<sub>2</sub> as illustrated above. In fact, X-ray diffraction confirms the prediction that this kinetically controlled structure-directed (templated) polycondensation defeats the thermodynamic tendency of the titanium dioxide to crystallize, resulting in a TiO<sub>2</sub> product that is amorphous. Thus, conversion to the crystalline phase for semiconductor applications requires thermal annealing, a process we optimized (Sumeral et al, 2003).

#### **Biomimetic Nanofabrication of Optoelectronically Active Materials:**

We discovered that the silicatein biomimetics described above also can be used to direct the synthesis of photoluminescent quantum dots and unique microlasers. With support from JPL and MURI, a collaboration was initiated between JPL and the Stucky research group in the Department of Chemistry at UCSB to investigate the feasibility of a new approach to science and planetary protection through nanotechnology. The use of QD's (Quantum dots) as tags to mark the presence of organics and organisms and to differentiate them from non-terrestrial organic material was explored.

Our preliminary studies have led to a new low temperature approach to preparing quantum dots, which would allow different compositions, sizes and luminescent properties of QD's to be explored. These QD's were functionalized with linkers for attachment to gram negative and gram positive bacteria. Perhaps most striking, it was demonstrated that water

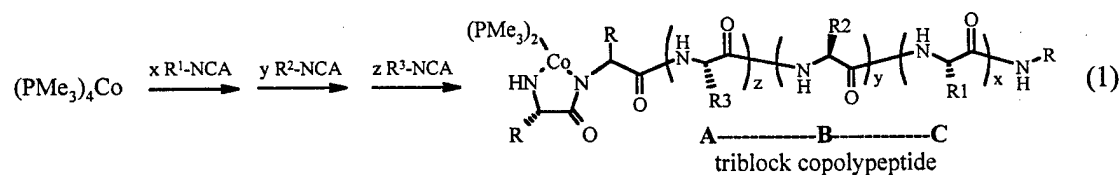
soluble quantum dots, with high quantum efficiency (> 25%) could be made that rapidly enter living cells, such as *E. Coli*, and organize in a site specific way within the cell.

A design strategy to constructing novel materials from nanoparticles and synthetic biopolymers has been developed during this period. Block copolypeptide polymers with specific binding affinities to metals, metal chalcogenides, metal oxides, or organics, are used to arrange nanoparticles (composed of metals, metal non-oxides, metal oxides, or organics) into well-defined, aggregated structures that are 2-4 orders of magnitude larger than the constituent nanoparticles. These materials are composed of nanoparticles of **two or more** compositions and the copolypeptide polymer. They have unusual organized microstructures, such that nanoparticles of one composition are spatially oriented completely interior or exterior to nanoparticles of a second composition. They have unusual aggregate morphologies, such as spheres, "apples" and "donuts." The sphere- and apple-shaped aggregates do not contain nanoparticles in the interior, and maintains their hollowness even upon combusive removal of the copolypeptide organic at temperatures to 800 C. These robust materials are anticipated to have great promise in applications that require surface catalysis, magnetic/electronic/optic properties, transport capabilities, and combinations thereof, such as catalysis, MRI, drug delivery, and sensors.

#### Development of initiators for hybrid multiblock copolypeptide Lustrin mimics:

The chemical synthesis of high molecular weight polypeptides is most directly accomplished by the ring-opening polymerization of  $\alpha$ -aminoacid-N-carboxyanhydride (NCA) monomers. NCAs are readily prepared, typically in a single step from commercially available amino acids, and polymerize in the presence of nucleophiles or bases to give polypeptides in good yield without racemization of chiral centers. In this area, we have developed highly effective, transition metal initiators for the controlled polymerization of NCAs into high molecular weight polypeptides (eq. 1) and have identified the active propagating species in the polymerization (Deming, T. J. and Curtin, S. A. *J. Am. Chem. Soc.*, 2000, 122, 5710-5717; Deming, T. J. *J. Polym. Sci. Polym. Chem. Ed*, 2000, 38, 3011-3018). Our organonickel complexes are able to produce polypeptides with narrow molecular weight distributions and controlled molecular weights. By addition of different NCA monomers, we are also able to prepare block copolypeptides of defined sequence and composition.

In related work, the Deming group has developed and synthesized nickel initiators which allow the preparation of hybrid block copolymers that contain conventional polymer domains interspaced between the block copolypeptide components (Curtin, S. A. and Deming, T. J. *J. Am. Chem. Soc.*, 1999, 121, 7427-7428). This chemistry allows us to incorporate inexpensive, commercial polymers (e.g. polyethyleneoxide, polystyrene, or polydimethylsiloxane) into our self-assembling block copolypeptides. These materials will be very useful in making a transition



from biological to more synthetic composite self-assembly processes useful for practical

applications. Our target has been to develop block copolymers containing elastomeric and self-assembling domains similar to the protein lustrin, found between the  $\text{CaCO}_3$  tablets of the abalone shell. This protein has been shown by the Hansma and Morse groups to provide strength to the abalone shell by possessing multiple domains capable of reversibly unfolding and refolding when stressed.

We have been developing the synthetic materials to mimic this protein through the design and synthesis of block copolypeptides. This past year, we have developed new amino acid residues based on ethylene glycol-modified serine that, for the first time, allow the efficient synthesis of high molecular weight beta-sheet forming polypeptides (Hwang, J. and Deming, T. J. *Biomacromolecules*, in press). This new technology has been used to construct block copolypeptides containing both flexible and self-associating domains modeled after structural protein motifs. We have prepared model block copolymers where non-associating random or helical structured domains are connected to the beta-sheet forming serine-containing polymers to study their self-assembly characteristics. We have found that the assembly of the beta strands greatly alters the packing of helical poly  $\gamma$ -benzyl-L-glutamate domains and that assembly can be controlled by varying the amount of water present in the material. We have also prepared block copolypeptides of the beta-sheet forming serine domains with random coiled polyelectrolyte or hydrophobic domains. Studies on the self-assembly of these polymers in either aqueous or organic solvents are currently underway to determine the parameters that control their association and dissociation. This knowledge will be used to fine tune these sequences to obtain mimics that can start to reproduce the mechanical behavior of lustrin.

#### **Biomimetic Syntheses with Silica and Other Network-forming Polymetallo-Oxanes:**

We previously reported the discovery and characterization of the silicateins, proteins that catalyze and spatially direct polymerization of silica in a marine sponge. Gene cloning, sequence analysis and 3-d molecular modeling allowed us to identify the mechanism of action by which the silicateins catalyze polymerization of silica, methyl- and phenylsilsesquioxanes (silicones) from the corresponding silicon alkoxides at neutral pH and low temperature. Genetic engineering has now helped us identify the structural determinants within the protein molecule that are responsible for this catalysis. Based on these results, we have used the new method for block copolypeptide synthesis developed by our colleague, Tim Deming (see immediately above), to synthesize defined diblocks that are truly biomimetic: they catalyze the polymerization of the silicon alkoxides at neutral pH, while simultaneously directing the structure of the polymerized material. As we published in *Nature*, when we allow the diblocks to form multimolecular concatenates, they direct the synthesis of long fibrillar bundles of silica; when we block this concatenation, transparent glassy spheres are produced.

The microphase separation and domain-partitioning principles that we have studied in biomineralization processes are being further exploited in the synthesis of hierarchically structured mineral-organic composites with defined order and disorder on multiple length scales. The organic organizers include hydrophilic-hydrophobic block copolypeptides (Deming; cf. above) and block copolyesters. A systems approach combining synthesis with microcapillary processing and soft lithography in a minimal number of device fabrication steps has been used to create optical devices. The soft lithographic fabrication of a dye-doped mesostructured silica ridge waveguide distributed feedback laser has been demonstrated. Fabrication of the ridge

waveguide DFB master and stamps suitable for soft lithography were accomplished by hierarchically patterning a photoresist. This simple technique removes previous requirements for etching and or metal deposition. Stamps made from these photoresist masters are then used to pattern rhodamine 6G-doped mesostructured silica capable of lasing (fwhm line widths of  $< 0.3$  nm, at pump intensities higher than  $\sim 55$  kW/cm<sup>2</sup>). Ring microlaser systems have been created that lase with pump intensities ca. 2 orders of magnitude less at  $\sim 0.25$  kW/cm<sup>2</sup>. This advantageous performance results from the ability to incorporate high densities of optical species in the highly organized mesostructures without aggregation and optical quenching. The high surface area and tunable pore size of the meostructures also has been shown to make them excellent chemical sensors.

#### **New Silica- And Metal Oxide-Organic Composite Materials. New Synthesis Strategies, Optical Waveguides, Micro-Lasers, And New Catalytic Materials:**

We developed benchtop synthesis paradigms that mimic nature's ability to create hierarchically structured and functional composite materials through assembly processes that are self-correcting and that dynamically organize space and function on all length scales. The approach is to unite biology, polymer, organic and inorganic chemistry for biomimetic and bioprocessing strategies that result in the practical synthesis of functional materials. Based on insights into the biological mechanisms and identification of key proteins that (1) are responsible for control of crystal phase, morphology, and dimensions and organization in the assembly of abalone shells (Belcher et al., *Nature*, 1997; Smith et al, *Nature*, 1999; Thompson et al., *J. Biopolymer Res.*, 1999) and (2) both catalyze and structurally direct the polymerization of silica and organosiloxanes (Cha et al, *PNAS* 1998; *Nature*, 1999; Shimizu et al., *PNAS*, 1998; Zhou et al., *Angew. Chemie*, 1999; Morse, *Trends in Biotechnol.*, 1999), new synthetic approaches to the control of mass transport, thermodynamic and chemical reaction processes (including both equilibrium and non-equilibrium processes) have been developed to produce complex multicomponent materials with structural control extending over length-scales ranging from the atomic and nanoscale to the macroscopic. Where we found biology uses templating, cooperative interactions and catalysis-control to regulate the nanostructure of biomineralized composites, we have similarly used templating, cooperative interactions and catalysis control; where biology uses stencils, molds, chemical fields or gradients and transport-control to determine the macrostructure of biomineralized composites, we are using micromolding, concentration gradients, exogenously applied fields (magnetic, hydrodynamic, chemical potential, and electrical) to achieve macroscopic ordering in new biomimetic materials.

#### **Synthesis Results:**

The biomimetic synthesis approach that we have used is based on nature's use of kinetic control, competing non-equilibria and equilibria phenomena, multiphase media and the organic/inorganic interface to synthesize composite materials with control of structure and physical properties from the nanometer to the micron scale. Lessons learned from the organic/inorganic interface control used by nature to sculpt the high lattice energy abalone shell architecture have led to a whole new class of crystalline zeolite-type phases with high charge density structures and a large variety of compositions including transition metal rich structures. Organic/inorganic interface considerations relative to the kinetics and thermodynamics of silica polymerization in biosilicate species has generated a new class of highly processible,

hierarchically patterned composite materials. Insights into the mechanisms used by living organisms to synthesize and process silica under environmentally benign conditions, while elegantly controlling silica morphology and patterning over multiple length scales, have led to the exciting new silica processing strategies described below.

Block-like biopolymers are used extensively in nature to direct spatial definition, interface and transport properties in biogenesis. We have shown that this principle applies equally well for the in vitro synthesis of inorganic/organic composites of a wide range of main group and transition metal oxide compositions (Stucky, Chmelka). Utilizing information provided by detailed biological investigations of silica sponge spicules, polypeptide block polymers (Deming, Morse, Stucky) have been designed that accelerate the hydrolysis of silicon alkoxides and hence their polymerization under neutral pH conditions. As described in detail in two of the sections that follow below, selected block copolymers can be used to generate specific macroscale morphologies. This is an important break-through in silica processing chemistry, and during the coming funding period the molecular mechanism of this reaction will be studied in detail and the scope of the control expanded.

We have found – in both our biological and biomimetic investigations – that the dynamics of biosilica assembly require a "soft" interface to cooperatively organize the polymerizing silica into intricate 3-d network structures. Thus, we (Chmelka, Stucky) demonstrated that hierarchically structured materials with organized nanostructured domains and defined macroscale morphologies are synthetically accessible through the use of organized organic domains with comparatively weak inorganic-organic interfacial interactions [e.g., hydrogen-bonding between bridging anions ( $\text{Cl}^-$  or  $\text{Br}^-$ ) and cationic surfactant and cationic silica species; or between non-ionic block copolymers and cationic inorganic species]. Recent examples include the use of emulsions, latex spheres, fluid-sol, di-, tri- and star di-block copolymers to give (1) transparent mesoporous spheres and monoliths ( $\leq 500 \mu\text{m}$  in diameter); (2) mesoporous fibers ( $> 500 \text{ mm}$  in length); (3) ordered cage and channel films ( $\text{cm} \times \text{cm}$ ) with low or high dielectric properties; (4) hollow and continuous spheres ( $< 1\text{-}100 \mu\text{m}$  in diameter) with well-defined patterned mesoporous walls; (5) monodispersed pore sizes in mesoporous (to  $> 400 \text{ \AA}$ ) phases with pore volume fractions as high as 0.85; and (6) hierarchically patterned (10nm - 100nm - 1000nm or greater) materials made of both main group and transition metal oxide (including mixed metal oxide) compositions. The precision and definition of the resulting 3-d structuring is remarkable, as recently confirmed by transmission electron microscopy (1.25 MeV) research in collaboration with Professor Osamu Terasaki of Tohoku University in Japan. Several new mesopatterned structural phases have been found.

We reported the first use of amphiphilic poly(ethyleneoxide)-poly(propyleneoxide)-poly(ethyleneoxide) (PEO-PPO-PEO) triblock copolymers to organize inorganic oxide networks. This paper (Zhao et al., *Science*, 279, 548, 1999) has been among the heavily cited papers in the chemical sciences over the past year, ranking 6<sup>th</sup> according to a citation index recently published by *Science Watch*. The significance of this work lies in its demonstration of the opportunities provided by block copolymer surfactant species for preparing mesostructurally ordered composites and porous solids with larger ordering length scales and, especially, substantially greater control over macroscopic material structures. This is possible because of the increased compositional and architectural diversity, larger molecular weight, and greater processibility of block copolymers compared to the low-molecular-weight surfactants used previously. The PEO-

PPO-PEO species, along with the block copolypeptides being prepared by Prof. Deming, are simple synthetic analogues of the more complex proteins, lipids, and other amphiphilic biomolecules used by the silica-forming species discussed above. The processibility of the silica/PEO-PPO-PEO system has allowed a range of new materials to be prepared with macroscopic morphologies in the form of powders, films, fibers, and bulk monoliths, which can be tailored to different applications. These include high-pore-volume catalysts and supports, functionalizable separation adsorbents for large molecules, low-dielectric-constant materials, chemical and biosensors, optical materials (including nano-lasers), robust semi-permeable coatings and packaging materials, etc. Progress highlights include:

#### **Synthesis of Transparent Crack-Free Silica/Block-Copolymer Composite Monoliths, with High Mesoscopic Order and Large Ordering Domains:**

A detailed study of the molecular and mesoscopic compositions and structures of these materials from our groups was recently published in *Macromolecules* (N. Melosh et al., *Macromol.*, 32, 4332, 1999). In this paper, nanophase-separation of the PEO and PPO copolymer blocks was established using solid-state two-dimensional (2D) heteronuclear correlation NMR techniques and correlated with the degree of mesoscopic ordering measured using X-ray diffraction (XRD) and transmission electron microscopy (TEM) for a systematically varied range of material compositions. Subsequent 2D XRD analyses of a transparent silica/PEO-PPO-PEO monolith with a high degree of mesoscopic organization has shown for the first time that large (2 cm!) single-crystal-like domains exist in the sample. These two properties of the composite monolith, transparency and nearly perfect anisotropic ordering over macroscopic length scales, have opened new opportunities for these materials in optical applications. Such prospects include the doping of optically active dye molecules into the hydrophobic regions of the composite at substantially higher concentrations than can be introduced in conventional (hydrophilic) sol-gel-derived glasses. Such higher dye concentrations yield enhanced optical sensitivity, while the block copolymer species prevent phase-separation of the hydrophobic dye, thus preserving material transparency. Secondly, compared to exclusively organic dye-containing polymers, the mesoscopically ordered silica framework provides significantly greater thermal and mechanical stabilities to the composite system. Following Prof. Chmelka's visit in February to Wright-Patterson Air Force Base, hosted by Dr. Thomas Cooper (a member of our MURI advisory board), their groups are collaborating on the development of new optical limiting materials, including porphyrin-doped transparent silica/PEO-PPO-PEO monoliths. Materials prepared and characterized at UCSB have been tested at WPAFB and shown to possess promising optical limiting properties, which are currently being examined. Incorporation of optically active oligomeric and polymeric species, such as poly(phenylene vinylene), is also underway. In particular, efforts are being directed toward the introduction of optical guests in oriented mesophase composites prepared using surface, shear, or magnetic fields or by annealing large single-domains, as mentioned above.

#### **Development of Hierarchically Ordered Composites and Porous Oxides for New Optical Waveguides and Micro-Lasers:**

We have taken advantage of the high lumiphore concentrations that can be loaded within the ordered channels of the our new mesoporous materials, in conjunction with the facile processibility of these materials, to produce micro-patterned waveguides, photonic structures and

microlaser arrays on silicon wafers (Yang, et al., *Science*, 282, 2244 1999; Marlow, *Adv. Mater.* 11, 632; 1999). Our long-range goal is to use these elements in the design of integrated optical or electro-optical chips. As we introduced last year and since published in *Science* (Yang et al., *ibid.*), we combined sol-gel/block copolymer self-assembly, templating with monodisperse latex spheres, and microcontact-surface patterning to prepare composites and porous oxide thin films with discrete and independently adjustable ordering length scales of 10 nm, 100 nm, and > 1 micron. This strategy is very general and can be used to form such hierarchical structures using essentially any sol-gel-derived network-forming metal oxide (Yang et al., *Nature*, 396, 152, 1998). We demonstrated that these surface-patterned silica/PEO-PPO-PEO mesophase composites display efficient optical waveguide properties and, when doped with Rhodamine-6G dye molecules, amplified spontaneous emission additionally occurs (Yang et al., *Science*, 282, 2244 1999); the result is an array of highly ordered, highly parallel micro-lasers. We also have demonstrated similar amplified spontaneous emission properties in self-assembled silica/cetyltrimethylammonium (a low-molecular-weight surfactant) microfibers doped with Rhodamine-6G (F. Marlow et al., *Adv. Mater.* 11, 632, 1999). These materials are excellent candidates for new classes of micro-laser array devices for fast, addressable, integrated optical circuits and optical displays. These and other optical possibilities being explored with supplemental support from the Semiconductor Research Corporation (SRC) and Motorola.

#### **Ultra-Low Dielectric Thin Films, Catalysts and Separation Media:**

We discovered that some of the best candidates for ultra-low dielectric coatings for microelectronic chips are mesoporous thin films synthesized using the acid-based block copolymer silica chemistry discussed above (Zhao, et al., *Science*, 279, 548, 1998; *J. Am. Chem. Soc.*, 120, 6024, 1998; *Adv. Mater.* 10, 1380, 1998). Mesoporous-macroporous materials have been obtained using multiphase single system solution chemistry (Zhao, et al., *Chem. Mater.* 11, 1174, 1999), making it possible to simultaneously maximize space flow velocity and accessible surface area for potential applications in catalytic and chromatographic separations.

#### **Bulk Porous Solids with Hierarchical, Independently Adjustable Pore Sizes in the Mesoscopic (5-20 nm) and Macroscopic (1-10 micron) Regimes. Applications for Sensors and Nanostructured Materials Synthesis "Factories" for New Materials:**

These materials are excellent candidates for new heterogeneous catalysts and separation adsorbents for large molecules: the large macropores allow fast diffusion and low resistance to mass transport, while the mesopores provide high reaction/adsorption surface areas. Such materials can be prepared by either a microemulsion-templating route (P. Schmidt-Winkel, *J. Am. Chem. Soc.*, 121, 254, 1999) or by kinetically stabilized droplet formation (D. Zhao, *Chem. Mater.*, 11, 1174, 1999). In related, low-molecular weight surfactant (MCM-41) materials, we have achieved the highest framework aluminum-loading yet demonstrated in aluminosilicate mesoporous solids (Janicke et al., *Chem. Mater.*, 11, 1342, 1999). This is important for increasing the catalytic activity of these materials, particularly with respect to their acid, ion-exchange, and/or adsorption properties. We are vigorously pursuing optimization efforts for these materials and expect soon to be measuring diffusion and reaction properties for them.

The beauty of this chemistry is the very facile, but selective processing that is possible in essentially single system configurations. The block copolymers are commercial grade, cheap



and can be recovered in high yields for subsequent new syntheses. The patterning is tunable throughout the biomolecular size domain so that size selective biomolecule separation or incorporation, attachment and packaging along with confined space biocatalysis are readily available with the synthesized ultra-large mesoporous phases that we have made during the past funding period. We are presently actively exploring protein separation and protein or enzyme encapsulation within these ultra-large pore phases.

In addition to obvious applications as sensors, the easy functionality of the wall surfaces of the mesopores makes them attractive as nanostructured chemical factories, as recently demonstrated (Aida, et al., *Science* 285, 2113, 1999) by the use of the highly ordered porous fibers mentioned above with a Ziegler-Natta catalyst supported within the mesopores to give highly oriented, high molecular weight, high density, crystalline polyethylene. The new synthesis strategies and materials we have developed provide numerous opportunities to explore and utilize chemistry in confined spaces (cages and channels). The nanostructured extrusion processing that is possible with these new materials can be expected to result in previously unattainable bulk properties for common polymers.

Additional applications of these materials are presently being explored in laboratories around the world. Usefulness of these applications is now in the "proof of concept" stage, and proposed as the focus for this sector of our team's research effort during years four and five of our MURI project.

**The Power Of Afm And Biotechnology Combined For Analyses Of Crystal- And Polymer-Based Composites. Applications To New Semiconductors, Lasers, Magnetic Information Storage Materials And Strong, Self-Healing Elastomeric Adhesives:**

**Crystal-Based Nanocomposites: Applications to New Semiconductors, Lasers and Magnetic Information-Storage Quantum-Dots:**

Prof. Hansma's development of atomic force microscope (AFM) and scanning ion conductance microscope technology led directly to a series of discoveries (in collaboration with Prof. Morse and Prof. Stucky) to reveal the previously unsuspected mechanism of formation of abalone shell nacre that underlies the enhanced fracture toughness of this microlaminate composite (Schaeffer et al, 1997; Fritz and Morse, 1998). In brief: Atomically coherent crystals of aragonite were demonstrated to form tapered conical stacks of truncated tablets by continual crystallographic growth through layers of fenestrated sheets of organic matrix, with the nanopores in these sheets acting like molecular stencils to guide the growth of the crystals from one layer to the next. The stochastic location of the nanopores generates the observed random lateral offset of successive nacre tablets, which ultimately generates the interdigitation of the aragonite tablets that contributes to the microlaminate's remarkable fracture toughness. This discovery has been cited by pioneers in the field of gallium nitride semiconductor production, who have developed a related method for the epitaxial growth of GaN through pores in a silica mask to filter-out crystal defects by lateral epitaxial overgrowth, thus obtaining crystalline domains with sizes sufficient for laser and semiconductor applications

Prof. Hansma's group has recently built an AFM that allows rapid imaging of biological processes in real time, and has used this new AFM in collaboration with the teams of Profs.

Morse, Brzezinski and Deming. We reached scan speeds of 104 lines per second, corresponding to an image every 1.2 seconds, allowing us to measure the critical step length of a growing calcite crystal in situ. With this microscope, we are now able to measure the precise interaction of the crystal-directing proteins that Dr. Michenfelder (in Prof. Morse's lab) has isolated and purified from the abalone shell. James Thompson imaged the changes induced by specific proteins on a growing calcite crystal. He and Dr. Michenfelder found that one of the proteins isolated from the abalone shell binds specifically to the step-edges of a growing calcite crystal, halting the growth of calcite. A second protein binds to the (104) crystallographic terraces, becoming occluded within the crystal. Acting in concert, these two proteins direct the transition from calcite to aragonite (revealed by Fourier-transformation of the AFM images to yield the two different atomic lattice patterns). The action of these two proteins thus appears to be sufficient to explain at the molecular level the "genetic switch" between these two polymorphs that we observed previously (Belcher et al., *Nature*, 1996). Preliminary evidence suggests that the terrace-binding protein is capable of directing the epitaxial nucleation of aragonite on the protein-modified lattice of calcite (Thompson et al., submitted to *Biophys. J.*, 1999). Cloning and sequencing of the cDNAs coding for the crystal-controlling proteins is now well underway, with two of the proteins fully sequenced. These efforts, in conjunction with 3-dimensional structural studies and modeling of the interactions with the crystallographic faces these proteins have been shown to control, will be used to identify the crystal-controlling structural motifs, and guide our efforts to design and synthesize effective biomimetics for this purpose.

In a potentially powerful new application of this discovery, we are using the aragonite-nucleating protein in a novel approach to fabricate nanoscale arrays of magnetic storage polycrystalline crystals (of Mn/Co/Eu-carbonate) that are isostructural with aragonite. We have shown that the use of these proteins provides a unique low-temperature route to the production of these valuable mixed metal carbonate crystalline materials, which otherwise are accessible only at high temperature. In collaboration with UCSB's Profs. Pierre Petroff (Computer and Electrical Engineering) and David Awschalom (Physics), we are working now to electrophoretically direct genetically engineered variants of the magnetic crystal-nucleating proteins into nanoscale arrays of crystallographically etched nano-pits in single-crystal silicon, and to use these anchored proteins for the orientationally controlled nucleation of magnetic nanocrystals. Confinement of the nanocrystals within the precisely etched facets of the nano-pits, and use of the uniformly anchored, genetically engineered proteins, should make it possible to precisely control magnetic nanocrystal location, spacing, magnetic domain size, atomic lattice orientation, and spin-state coupling. The objective is to produce nanoscale arrays of electronically addressable magnetic quantum dots for improved information-storage materials.

#### **Discovery of a New Class of Strong, Self-Healing, Modular Elastomeric Adhesive Polymers:**

Using a working prototype AFM, Prof. Hansma's group examined the force required to unfold and refold proteins. Through these studies we discovered a mechanism that nature uses to produce strong and tough fibers, adhesives, and composites (Smith et al. *Nature*, 1999). This discovery was patented, and received wide acclaim in the popular press. We discovered that the elastomeric adhesive protein that holds the minute crystals of aragonite together in the abalone shell nacre is a major key to the greatly enhanced fracture-resistance of this composite. This elastomeric adhesive, named "lustrin", was purified and characterized by Prof. Morse's group

(Shen et al., 1997). Analysis of the structure from the sequence of the cloned cDNA revealed that the protein is a unique modular polymer, built-up from many repetitive, modular domains. By pulling on freshly cleaved nacre with the AFM cantilever (using the instrument as a sensitive single-molecule strain-gauge), we observed the sequential (and reversible) unfolding of these modular domains in the organic elastomer at the mineral-organic interface. The resulting sawtooth-like force-extension curves, together with the observation that we could repeatedly unfold and refold the molecule(s) without touching the surface between pulls, suggest that "sacrificial bonds" bonds within the molecule are breaking and reforming. As Lustrin is present on that surface, it is possible that we observed unfolding of this protein. From these studies, we discovered that the mechanism behind the strength and toughness of an adhesive is revealed by the force-extension curves, and does not depend on the identification of the specific molecules involved. This behavior may reflect the successive opening of intra-chain loops or folded domains within a single molecule, or the successive release of sacrificial inter-chain bonds holding a crosslinked multichain matrix together. We now are collaborating with Prof. Deming's group to produce biomimetic strong and "self-healing" elastomeric fibers based on nature's design, first revealed in these studies of the abalone shell protein (see final section below).

Rapid AFM imaging (with ultra-short, ultra-fine and ultra-sensitive cantilevers of our patented design) also has allowed us to measure biological processes in real time. We are making new prototype microscopes with NSF support that we plan to use for obtaining fast images of processes related to biomineralization. For example, the new high-speed/ high-resolution imaging of single molecules will allow us to analyze nascent synthetic polymers developed in Dr. Deming's group.

#### **Mesoscopically Ordered Block-Copolymer-Silica Monoliths, Thin Films, and Fibers:**

The use of block copolymers to produce aligned and/or transparent block-copolymer-silica monoliths, thin films and fibers with high degrees of mesoscopic order has opened promising application opportunities in opto-electronics. Important new features and properties of these materials include:

1. Transparent monoliths and thin films with high degrees of mesoscopic organization over large domains;
2. Large mesoscopic ordering length scales with regions into which optically active or conducting guest species can be selectively incorporated. Often such molecules can be introduced in substantially higher concentrations than possible in homogeneous blends, which are typically limited by the solubilities of, for example, organic dyes in transparent sol-gel matrices;
3. Alignment of films and fibers under conditions of shear flow, which allows inorganic-organic composites and mesoporous materials to be produced with high degrees of orientational order. Transparency is preserved even after calcination for thin films less than 1 micron thick.

Chmelka's group has examined in detail the molecular and mesoscopic structures of a series of transparent poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO)-silica composites (Melosh *et al.*, *Macromolecules*, submitted). Important mechanistic insights from this work are being used to develop processing conditions for incorporating organic dyes and conducting/light-emitting polymers into the transparent inorganic-silica monoliths. For example, we are adding porphyrin dye species to block-copolymer-silica synthesis mixtures produces bright yellow transparent monoliths with potential optical filter applications. (The porphyrin species were provided by Dr. Tom Cooper, Wright-Patterson AFB, a member of our MURI Scientific Advisory Panel and a participant in our 1997 review.) In addition, hydrophilic poly(ethylene dioxythiophene) poly(EDOT), a conducting polymer, has been incorporated into mesoscopically ordered transparent block-copolymer-silica composites and thin films; the electro-optical properties of poly(EDOT) make these materials attractive as coatings for "smart window" applications. Introduction of derivatives of poly(phenylene vinylene) (PPV), a well-known light-emitting polymer, into these composites is underway, motivated by display and sensor applications. Under appropriate conditions, these mesoscopically ordered composites or mesoporous solids, with or without molecular guest additives, are processable as oriented films on dip- or spin-coated substrates and as free-standing fibers.

Numerous interfaces exist in these areas with U.S. Army research laboratories at the Aberdeen Proving Grounds, Maryland, especially with the Polymers Research Branch, as discussed by Prof. Chmelka, Dr. Richard Schuford (Branch Chief), and other APG staff during Prof. Chmelka's recent visit there. Discoveries at UCSB appear relevant to a broad range of diverse application interests at APG, notably in the areas of protective or transparent coatings/membranes, composite or porous metal oxide fibers, nanoceramics and metal interfaces. Capabilities for bulk material processing and characterization/testing at APG provide excellent complements to facilities and expertise at UCSB. At the invitation of Dr. Schuford, efforts will be made to incorporate APG resources into the development and testing of UCSB materials for these and other applications of interest to the Army.

#### **Hierarchical Ordering of Inorganic Oxide Materials:**

Stucky's and Chmelka's groups have very recently extended their procedures for synthesizing inorganic-organic mesophases, using emulsion processing or micromold patterning of these materials to create hierarchical structural order over macroscopic length scales. The significance of these advances is that they allow, for the first time, the design and preparation of multifunctional composite structures with well-defined structural order from nanometer to centimeter length scales. This is analogous to the exquisite control of  $\text{CaCO}_3$  biomineralization by marine mollusks and  $\text{SiO}_2$  organization exercised by diatoms and siliceous sponges analyzed by our groups, and the mechanisms we have used to achieve this hierarchical control of inorganic-organic structural organization over several orders of magnitude in materials synthesis bear a fundamental relationship to those we have uncovered in the biological systems. Progress in these areas includes the following recent results:

1. Development of a simple procedure for preparing hierarchically ordered structures by combining (concurrently or sequentially): micromolding; templating with latex spheres; and cooperative self-assembly of hydrolyzable inorganic species (metal alkoxides, metal

chlorides) and amphiphilic block copolymers. The resulting materials exhibit structural ordering over multiple discrete length scales, *e.g.*, 10 nm, 100 nm and 1000 nm (with additional control to the scale of centimeters; cf. below. We have further controlled the physical properties of these materials over a wide range, by versatile modification of their chemical compositions and ordering length scales, which are independently tunable;

2. Use of block-copolymer-stabilized microemulsions to produce organized macropores with mesoscopically ordered inorganic oxide wall structures. Uniform, concentrated oil-in-water microemulsion droplets with a narrow size distribution lead to materials with uniform three-dimensionally continuous macropores (*ca.* 36 nm in diameter). The macropore walls are comprised of highly ordered hexagonal arrays of mesoscopically ordered (*ca.* 12 nm) porous silica. The ordering length scales are independently adjustable in these high-surface-area materials (which have been given the name siliceous "mesocellular foams", MCFs);

3. Use of kinetically-frustrated macrophase separation to form droplets of a concentrated aqueous electrolyte solution, around which highly ordered mesoporous metal oxides are organized. Such droplets are formed as a result of phase separation induced by solvent evaporation or inorganic oxide gelation and can be prevented from coalescing by the high viscosity of the block-copolymer/sol-gel mixture. Substantial control can be exercised over the average sizes of the resulting macropores, which tend to form foam-like structures resembling the spicules of the siliceous sponges whose analysis we describe below.

The micromold processing techniques are being pursued in collaboration with Professor George M. Whitesides (Harvard University) and are producing promising device applications. In particular, the patterning of mesoporous silica films is an important advance for their use as low-dielectric-constant (*k*) materials in increasingly miniaturized integrated microelectronic circuits. High porosities (*ca.* 80%) and orientational ordering of hexagonal mesoporous silica (which can be aligned with the long axes of the aggregates in the plane of a dip-coated substrate) allow materials with dielectric constants of *ca.* 1.4 to be produced, an approximately 30% improvement over existing low-*k* materials. Furthermore, with the high degrees of macropore ordering achievable on dimensions of 100-1000 nm, opportunities also exist for developing novel photonic band-gap properties in these materials. In addition, orientationally ordered films of 3D cubic mesostructured oxides can be produced that allow the diffusion of guest molecules to access the underlying substrate; this allows such materials to be useful for membrane separations and sensors. Micromolding of these materials using lithographically etched polymer stamps allows inorganic-organic thin films to be macroscopically patterned into features with micron-size dimensions and fidelity over centimeter length scales for device applications.

#### **From Biology to New Materials Synthesis:**

Our use of multiple phases in microemulsion or macrophase-separating systems to control inorganic oxide structures over different length scales is analogous to the processes used by Nature in the control of biosilicification (see below). For example, silica concentration, organization, and deposition occur in diatoms in the silica deposition vesicles, which are intracellular compartments that are macroscopically segregated from the rest of the intracellular

contents, the cell membrane (a lipid bilayer), and the external growth medium. We are exploring these relationships and their control of mass transport, self-assembly/organization and polymerization of molecular species into hierarchically ordered inorganic-organic structures. Similarly, where we found that biology uses templating, cooperative interactions and catalysis-control to regulate the nanostructure of biomineralized composites (see below), we have used templating, cooperative interactions and catalysis control (described above); where biology uses stencils, molds, chemical fields or gradients and transport-control to determine the macrostructure of biomineralized composites, we are using stencils, molds, and exogenously applied fields (magnetic, hydrodynamic, chemical potential, electrical) to achieve macroscopic ordering in new biomimetic materials (as described above, and in last year's report). Coupling insights across the broad interfaces joining biology, chemistry, physics and engineering is allowing us to control material composition and structure in heretofore unforeseen ways. Investment in understanding the molecular mechanisms and foundations of these complicated systems is providing the enabling insights from which the new material properties, processes, and device functions described above are being realized.

### **Silicon Transport and Intracellular Processing by Diatoms:**

Understanding the solution-phase biochemistry used by diatoms and sponges is crucial for developing both environmentally friendly materials processing strategies and procedures for controlling material structures over a hierarchy of length scales. In our surfactant and block-copolymer-based material syntheses described above, extremely acidic (pH 1) or alkaline (pH 13) conditions at temperatures typically above 100 °C are needed to produce ordered silica-organic composites. In contrast, diatoms and siliceous sponges concentrate, assemble, and deposit silica under substantially milder ambient conditions (pH ~ 7-8; temperatures 0-28 °C). The recognition of silicon species by transporters, intracellular carriers and polymerization-controlling interfaces is being investigated in a collaboration between the groups of Profs. Chmelka, Brzezinski and Morse and Dr. Hildebrand (at UC San Diego). To probe these processes *in situ* in living diatoms, Chmelka's laboratory has developed a one-of-a-kind NMR probehead with a uniquely large-coil-volume design for measuring the extremely dilute soluble <sup>29</sup>Si species present in living diatoms. This is among the largest solenoid coils (*ca.* 30 mm in diameter) ever made for high resolution NMR spectroscopy analyses; the essential feature is a novel winding design for preserving the high magnetic field homogeneity required. Preliminary measurements have demonstrated the feasibility of using this unique device for measuring dissolved <sup>29</sup>Si species with concentrations ≤500 μM. Based on the work of Brzezinski and Hildebrand, such species in living diatoms are expected to include silicic acid and possibly ionophore complexes or other dissolved intracellular silica-organic species. Measurements are underway on densely packed diatoms and will soon be extended to a flow-through steady-state bioreactor system for analyses of silicon transport and speciation in living diatoms.

Diatoms must quickly take up enough silicon from the environment to fabricate a complete cell wall in a short time (less than 1 hr in some species), but must prevent the silicon from prematurely polymerizing in the cell until it is transported to the silicon deposition vesicle (SDV). By understanding the nature of the recognition and interaction of the silicon species with the responsible components of the cell's machinery, we hope to gain insights useful in novel approaches to the control of silicon speciation for materials synthesis. Dr. Hildebrand, whose

pioneering cloning and characterization of the silicon transporters we reported last year, has now discovered a silicon concentration sensing and control mechanism in diatoms. He has found that silicon uptake is controlled by the rate of incorporation into the cell wall, and not by extracellular silicon levels. In spite of the relatively large amounts of silicon that are taken up and effluxed from the cell during cell wall synthesis, the intracellular soluble pool levels change very little, and very gradually. Accurate measurements reveal that these pools are significantly more concentrated than the normal threshold for polymerization of silicic acid. This strict control over intracellular pool levels, and the maintenance of intracellular concentrations above the polymerization threshold, both reveal the activity of an as-yet unidentified silicon-binding molecule. From our results, we propose that the ratio of silicon to silicon-binding components are what controls uptake and efflux. The tight control over the soluble intracellular silicon pool level couples silica synthesis to the uptake of the precursor. This new discovery fundamentally changes the contemporary understanding of diatom cellular silicon metabolism: Although external silicon availability is required for silica synthesis, it is not the driving force. Because of the internal sensing and control mechanism, silicon is drawn into the cell upon demand, thus allowing greater control over intracellular processing. Brzezinski's lab completed their studies of the chemical form of silicic acid transported by diatoms. Last year we reported that our initial results refuted the widely accepted thinking (and the current literature) that marine diatoms transport silicon into the cell in the form of the anionic  $\text{SiO}(\text{OH})_3^-$ . The original view was derived from studies of an atypical diatom that can grow without depositing Si in its cell wall. In studies of the pH dependence of silicic acid uptake in four species of diatoms, Dr. Yolanda Del Amo found that the form of Si transported is the undissociated silicic acid for all species except the unusual one, and has identified the source of error in the original studies with that species. These results also reveal that the transport process is actively regulated by a recognition process.

Dr. Hildebrand's lab completed its molecular characterization of the silicon transporters in diatoms. Analyses of the cloned DNAs coding for the transporters revealed that the carboxy-terminal portion of all five silicon transporters found in one cell probably form "coiled-coils", protein structures typically found to interact with other proteins. We suspect that this interaction is the key to the regulation of silicon transport described above, providing a means for controlling the silicon transporters in response to the sensing and control mechanism we have identified. Genetic and proteins engineering methods similar to those described above are now being pursued to identify (i) components of the sensing and regulatory mechanism controlling the transporter proteins, and (ii) the structural determinants on the transport molecules that govern their recognition and transport of silicon. Other cellular transporters have shown to modify the species they transport. Thus, our analyses of the interactions of the silicon transporters may provide new insights into mechanisms controlling silicon reactivity.

Brzezinski and Hildebrand collaboratively determined the roles of the different silicon transporters. Future plans include development of a recombinant DNA vector for amplified synthesis of the transport protein in yeast, to enable a detailed examination of the transport behavior of each transporter using the radiotracer  $^{32}\text{Si}$  (produced by a method developed and patented by Prof. Brzezinski and D. Phillips at Los Alamos national Laboratory). The recombinant DNA-expression system also will be used to investigate the active site for Si recognition and transport in each transporter protein, using NMR with  $^{13}\text{C}$ -labeled transporters and  $^{29}\text{Si}$  substrate, in a collaboration between Brzezinski, Chmelka and Hildebrand. Participants from the laboratories of Brzezinski, Hildebrand and Stucky have initiated studies to isolate and

characterize the intracellular Si-ionophores and organic conjugates of silicon from diatoms. These molecules are thought to act as organic carriers, capable of transporting silicon by modification of solubility of and polymerization activity of Si. This effort was facilitated by the mass-cultivation system developed for this project by Brzezinski's laboratory, which has successfully grown over 100 g of a silicified diatom - an enormous quantity by previous standards.

#### **In Situ Calcite Crystal Growth Experiments with Biopolymers from Coccoliths and Abalone Nacre:**

Coccolithophores are unicellular algae approximately 10  $\mu\text{m}$  in diameter that produce exquisitely nanostructured scales or plates (called coccoliths) on the exterior of the cell. The coccoliths represent the only known biomineralized structures produced intracellularly and transported extracellularly *via* exocytosis. The coccoliths of *Pleurochrysis carterae* are approximately 1  $\mu\text{m}$  in size and consist of multiple structures composed of two morphologically distinct subunits, A and B, each of which diffracts as a single calcite crystal. As in the case of other biomineralized structures (e.g. abalone shells), organic polymers (proteins and polysaccharides) are found in close association with the calcite crystals of the coccoliths. Each A and B subunit appears to have its own nucleation site, and independent post-nucleation crystal growth. As with the abalone nacre, the morphology is thought to be directed by the biopolymers. Comparison of the mechanisms controlling the pattern and growth of the coccolith subunits presents a useful system for analysis in concert with our ongoing work with the abalone nacre.

In collaboration between Prof. Hansma's lab with Prof. Paul Levine's group at Stanford, Prof. Morse's group and Prof. Stucky's group, we used the new AFM developed by Prof. Hansma to analyze (in real time) the effects of the polymers extracted from coccoliths on the growth of calcite crystals. Interestingly, the total unfractionated mixture of polymers from the coccolith produces similar changes in crystal morphology to those produced by the proteins from abalone nacre. Individual proteins purified from the two biomineralized materials produce very specific effects on crystal growth. Our results suggest that specific proteins from the coccolith interact differently with the inorganic components to produce the morphologically distinct subunits. These studies, in conjunction with analyses of the sequences of the individual proteins (being conducted in Morse's lab, via cloning and analysis of the corresponding cDNAs), structural analyses of the proteins by solution NMR (in Chmelka's lab) and 3-dimensional molecular modeling of the proteins using the new POINTER energy-minimization algorithms (developed by John Evans, a talented faculty member and applicant for an ARO Young Investigator Award at NYU, with whom we are collaborating closely), will facilitate the design and synthesis of polymers for use in the control of crystalline thin film materials (such as the magnetically active crystalline thin films we reported last year).

#### **Mechanism of Nacre Microlaminate Nanofabrication Discovered:**

Our studies revealed a new mechanism responsible for the control of the biological nanofabrication of the microlaminate composite of molluscan shell nacre. Our development and use of a series of new improvements in AFM technology led us to discover that the organization of this microlaminate is the result of the coherent growth of crystals through a network of



stochastically located nanopores in an array of fenestrated protein sheets that act as molecular stencils, guiding the growth of the crystals from one layer to the next (Schäffer et al., 1997). This mechanism of nanofabrication, and the consequent effects on the resulting composite, differ significantly from the previously accepted mechanism, which envisioned periodic termination of crystal growth limiting each lamina, followed by epitaxial nucleation at the start of each crystal layer. Our team's AFM analyses first revealed the atomic lattice coherence between vertically adjacent crystal layers; revealing that the "stacks" of crystal layers in the nacre are in fact uniaxial, suggesting the existence of direct connections via mineral bridges between the crystal layers. Development of the TappingMode AFM made it possible for us to observe the nanopores in the protein sheets through which these mineral bridges grow, and development of the Scanning Ion Microscope (SICM) allowed us to confirm that these nanopores are true, stencil-like fenestrations. These enabling developments in scanning probe microscopy that allowed us to image the nacre and protein samples without resorting to the methods of preparation (that often introduce artifacts in conventional electron microscopy) were complemented by developments on the biological side. By placing a cover slip between the abalone's mantle (the shell-secreting epithelium) and the shell, Morse's group was able to induce the animal to fabricate a "flat pearl", a conveniently analyzed sample of newly formed nacre. This simple model system made it possible for Morse's and Stucky's groups to analyze the proteins and minerals as they were sequentially deposited, and removal of the minerals from the flat pearls revealed the protein sheets for imaging with the AFM and SICM. AFM confirmed the identification of the nanopores in the interlamellar sheets, and the SICM, which measures ion flux through the sheets, revealed that these pores are sufficient for ion conductance. The size and spacing of the pores in the organic sheets correlates with that of protrusions found on the adjacent mineral tablets. Moreover, the pore-to-pore spacing and the stochastic location of the nanopores sufficiently account for the observed random lateral offset of successive nacre tablets, which generates the interdigitation of the aragonite tablets that contributes to the microlaminates great fracture toughness.

In the biological nanofabrication of the abalone shell and flat pearl, we previously showed that aragonite (001) is nucleated directly on a calcite (104) surface that acts as a "primer". Using the small proteins we extracted from these biologically produced minerals, we also demonstrated that we could duplicate this nucleation and phase transition *in vitro*, with perfect fidelity of the atomic lattice orientation to that produced biologically. This is interesting because aragonite is a thermodynamically unfavorable phase at room temperature. Further, the (104) face of calcite does not appear to be a particularly good template for the growth of aragonite. The ability to control crystalline phase in this way is one of the most unusual and potentially valuable features of biologically derived materials. It is possible to achieve near atomic resolution on calcite surfaces using the atomic force microscope. We used this capability to image the calcite (104) surface while it grows from a super-saturated calcium carbonate solution. We should be able to use this technique to determine the structure of the relaxed calcite (104) surface under the conditions found during nacre growth. We characterized the interaction of this surface with proteins purified from abalone nacre by Morse's group. AFM analyses of the interactions of these aragonite-determining proteins with the growing calcite interface at the molecular level (in conjunction with our molecular modeling studies described above) shed light on the mechanisms that control crystal phase, orientation and morphology in biologically produced composites, and suggest new ways to control these properties in biomimetic materials (Thompson et al., 2001).

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## INVENTIONS

"Amplification Of Dna's Intrinsic Blue Luminescence To Create A Fret-Based Sensor", Morse, Stucky, Cha, UC, McCutchen, Doyle are presently preparing to file for full US and International patent protection.

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"Methods And Compositions For Improved Binding Of Histidine-Containing Proteins To Substrates: (Pending. UC #2001-428) Morse, Stucky & Gaul.

"Methods And Sensors For Luminescent And Optoelectronic Detection And Analysis For Dna And Rna" (Pending. US # 09/836,579) Morse, Stucky & Cha

"Methods, Compositions and Biomimetic Catalysts for In Vitro Synthesis of Silica, Polysilsequioxanes and Polymetallo-oxanes." (Pending. US #09/856,599) Morse, Stucky, Deming, Cha, Shimizu & Zhou.

"Methods, Compositions, and Biomimetic Catalysts for in Vitro Synthesis of Silica, Polysilsequioxane, Polysiloxane, and Polymetallo-Oxanes" Daniel E. Morse, Galen D. Stucky, Timothy J. Deming, Jennifer N. Cha, Katsuhiko Shimizu, and Yan Zhou, Patent Disclosure 99-167-1, University of California System, December 1998 U.S. Provisional Patent Application Serial No. (UC case no. 99-167-2; USSN 60/112,944, patent pending 2001).

"Microfabricated Cantilevers with Pads and Method of Manufacture." P.K. Hansma. U.S. Provisional Patent UC Case #99-031-1.

"Modular, Energy-Dissipating Material and Method for Using It." J. Kindt, T. Deming, D.E. Morse, G.D. Stucky, and P.K. Hansma. Patent #6,376,636 B1.

"Self-Healing Organosiloxane Materials Containing Reversible And Energy-Dispersive Cross-Linking Agents" (Pending. US # 10/193,533) Harreld, Hansma, Stucky, Wong, & Morse

"Self-Healing Organosiloxane Materials Containing Reversible and Energy-Dispersive Crosslinking Domains." J. Harreld, M. Wong, P.K. Hansma, D.E. Morse, and G.D. Stucky. U.S. Provisional Patent UC Case #2001-409-1.

"Structure-Directing Synthesis Of Metal Oxides And Nitrides, Metalloid Oxides And Nitrides, Rare-Earth Oxides And Nitrides For Electronic And Other Applications". (Pending. UC # 2002-524) Morse, Sumerel and Stucky.

"Synthesis of a Family of Mesoscopically Ordered, Hydrothermally Stable, Ultra Large Pore Size Mesoporous Silicas and Transparent Silica-Organic Monoliths and Thin Films By Using Amphiphilic Block Copolymers" Galen D. Stucky, Bradley F. Chmelka, Dongyuan Zhao,

Qisheng Huo, Jianglin Feng, and Nick Melosh, Patent Disclosure 98-089-1 and U.S. Provisional Patent application, University of California System, October 23, 1998.

"Syntheses of Oriented Inorganic-Surfactant and Mesoporous Solids Using Liquid Crystal Processing Strategies," S.H. Tolbert, Firouzi, A., G.D. Stucky, and B.F. Chmelka. U.S. Provisional Patent application, submitted.

## **PRESENTATIONS**

### **Mark Brzezinski**

Nanoscale control of biomineralization in abalone, sponge and diatoms, Invited poster, American Geophysical Society Meeting, December 2000.

### **Brad Chmelka**

Royal Dutch Shell Laboratory, Catalysis Group, Amsterdam, The Netherlands, October, 1998.

University of Utrecht, The Netherlands, Dept. of Inorganic Chemistry and Catalysis, October, 1998.

Workshop on Molecular Processes in Zeolites, Amsterdam, The Netherlands, October, 1998.

U.S. Army Research Laboratories, Aberdeen Proving Ground, Maryland, September, 1998.

David and Lucile Packard Foundation Fellows' Meeting, Santa Fe, New Mexico, September, 1998.

Symposium on Magnetic Resonance in Zeolites, University of Leipzig, Germany, August, 1998.

Ecole Nationale Supérieure de Chimie, Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique, Montpellier, France, July, 1998.

Université de Pierre et Marie Curie, Laboratoire Chimie de la Matière Condensée, Paris, July, 1998.

Observatoire Français des Techniques Avancées, Paris, June, 1998.

Risø National Laboratory, Denmark, "Unifying Principles for Engineering Soft Materials," June 1998.

Material Research Society Symposium: Inorganic-Organic Composite Solids, San Francisco, April, 1998.

University of Notre Dame, Dept. of Chemical Engineering, South Bend, Indiana, April, 1998.

Centro de Investigación y Desarrollo, Dpto. Tecnología de Tensioactivos, Barcelona, Spain, March, 1998.

Symyx Technologies, Santa Clara, California, February, 1998.

National Science Foundation Workshop, "High Field NMR," Washington, D.C., January, 1998.

Rhodia, Aubervilliers, France, October, 1999.

Universit de Pierre et Marie Curie, Laboratoire Chimie de la Matire Condense, Paris, October, 1999.

Instituto Mexicano del Petroleo, PEMEX, Mexico City, April, 1999.

Massachusetts Institute of Technology, Dept. of Chemical Engineering, March, 1999.

University of Texas, Austin, Dept. of Chemical Engineering, February, 1999.

Ohio State University, Dept. of Chemistry, Columbus, Ohio, February, 1999.

Wright-Patterson Air Force Base, Laser Hardened Materials Group, February, 1999.

University of Colorado, Dept. of Chemical Engineering, January, 1999.

Instituto de Ciencia de Materiales, CSIC, Universidad de Sevilla, Spain, December, 1999.

Universitat de Barcelona, Departament de Química Orgànica, Barcelona, Spain, November, 1999.

Rhodia-Rhône Poulenc, Aubervilliers, France, October, 1999.

Université de Pierre et Marie Curie, Laboratoire Chimie de la Matière Condensée, Paris, October, 1999.

Phil Pincus Symposium, University of California, Santa Barbara, August, 1999.

Instituto Mexicano del Petroleo, PEMEX, Mexico City, April, 1999

Massachusetts Institute of Technology, Dept. of Chemical Engineering, March, 1999.

University of Texas, Austin, Dept. of Chemical Engineering, February, 1999.

University of Texas, Austin, Dept. of Chemistry, February, 1999.

Ohio State University, Dept. of Chemistry, Columbus, Ohio, February, 1999.

Wright-Patterson Air Force Base, Laser Hardened Materials Group, February, 1999.

University of Colorado, Dept. of Chemical Engineering, January, 1999.

Nanoscale control of biomineralization in abalone, sponge and diatoms, Invited poster,

American Geophysical Society Meeting, December 2000.

Cornell University, Department of Materials Science, December, 2000.

Royal Institute of Technology, Department of Chemistry, Stockholm, Sweden, November, 2000.

Genencor International, Central Research, Palo Alto, California, October, 2000.

JSR Corporation, Tsukuba Research Laboratories, Japan, August, 2000.

California State Polytechnic University, San Luis Obispo, Dept. of Chemistry, May, 2000.

Centro de Investigación y Desarrollo, Dpto. Tecnología de Tensioactivos, Barcelona, Spain, March, 2000.

Universitat Rovira i Virgili, Department of Chemical Engineering, Tarragona, Spain, March, 2000.

Universidad de Miguel Hernandez, Depto. de Tecnología de los Materiales, Elche, Spain, February, 2000.

Max-Planck-Institut für Kohlenforschung, Mülheim, Germany, February, 2000.

Johann-Gutenberg-Universität, Fachbereich Physikalische Chemie, Mainz, Germany, February, 2000.

### **Tim Deming**

ACS National Meeting, San Diego, CA, Synthesis of Polypeptides Using Transition Metal Initiators ACS Award in Polymer Chemistry Symposium, April 2001

Chemistry Department Seminar, Cal State Univ., Long Beach, CA, Synthesis and Self-Assembly of Block Copolypeptide Materials, May 2001

UCSB/TWAS Workshop on Materials, Trieste, Italy, Synthesis and Self-Assembly of Block Copolypeptide Materials, May 2001

Eindhoven, Netherlands, Synthesis and Properties of Block Copolypeptides Plenary Lecture, European Polymer Federation, July 2001 meeting

Bodega Bay, CA, Synthetic Polypeptide Adhesives MARBEC workshop, November 2001

Boston, MA, Synthesis of Polypeptides Using Transition Metal Initiators Knowledge Foundation Workshop, December 2001

University of Wisconsin, Chemistry Department, Madison, WI, Synthesis and Self-Assembly of Block Copolypeptide Materials, December 2001

National Meeting of the American Chemical Society, Chicago, IL, Biomedical Applications of Polypeptides . August 2001

Chemistry Dept Seminar, UC San Diego, CA, Self-Assembly of Block Copolypeptide Materials February 2002.

University of Washington, Chemistry Department, Seattle, WA, Synthesis and Self-Assembly of Block Copolypeptide Materials, February 2002

Institut Curie, Paris, France, Synthesis of Polypeptides Using Transition Metal Initiators Rothschild Fellow Lecture, May 2002

CNRS-UCSB-MRL Conference, Paris, France, Synthesis and Self-Assembly of Block Copolypeptide Materials, April 2002

Materials KJIST-UCSB Conference, Santa Barbara, CA, Synthesis and Self-Assembly of Block Copolypeptide, June 2002

### **Paul Hansma**

ACS Biological Applications of Nanotechnology Conference, "Molecular Mechanics of Single Protein Molecules Probed with the Atomic Force Microscope", Berkeley, CA. June 2001.

American Society of Mechanical Engineers Conference, "Molecular Mechanics of Single Protein Molecules Probed with the Atomic Force Microscope", Snowbird, UT. June 2001.

Scanning Tunneling Microscopy/Spectroscopy Conference, "Next Generation of Atomic Force Microscopes", Vancouver, Canada. July 2001.

ITP Program, UCSB, "The Next Generation of Atomic Force Microscopes", Santa Barbara, CA. November 2001.

California Institute of Technology, Chemical Physics Seminar, "The Next Generation of Atomic Force Microscopes", Pasadena, CA. November 2001.

UC Irvine Colloquium, "A molecular mechanistic origin of the toughness of natural adhesives, fibres, and composites: abalone shells and bone", Irvine, CA. January 2002.

UCSB Small Wonders, "Small Wonders of Evolutionary Engineering: From Abalone Shells to Bone", Santa Barbara, CA. May 2002.

Scanning Probe Microscopy, "Implications of Single Molecule Research for Real World Problems", Las Vegas, NV. May 2002.

7th International Conference on Nano-Scale Science and Technology and 21st European Conference on Surface Science, "Implications of Single Molecule Research for Biomedical Science and Applications: Collagen and Beyond", Malmö, Sweden. June 2002.  
Biomaterialization Gordon Conference, "Molecular mechanistic origin of the toughness of natural adhesives, fibres, and composites: from abalone shells to bone", New London, NH. August 2002.

### **Galen Stucky**

"Using Interfaces, Non-equilibrium and Multiprocesses for the Molecular Design of Materials from Å to cm", Stanford University Hopkins Marine Station, May 21, 1998

"Using Interfaces, Spatially Competing Domains, and Multiprocesses in the Molecular Design of Composite Materials", Air Products and Chemicals, Inc., Allentown PA, June 10, 1998

"Using Interfaces, Spatially Competing Domains, and Multiprocesses in the Molecular Design of Composite Materials", Lucent Technologies, Murray Hill NJ, June 9, 1998

"Using Interfaces and Competing Assembly Processes in the Molecular Design and Synthesis of Nanostructured Materials", Watt Centennial Seminar, University of Texas at Austin, April 28, 1999

"Using Interfaces and Competing Assembly Processes in the Molecular Design and Synthesis of Nanostructured Materials", Princeton Materials Institute, May 11, 1999

"Mesoporous Structures: A Review", Sendai University, September 26, 1999

"Using Interfaces and Competing Assembly Processes in the Molecular Design and Synthesis of Composite Materials", Texas A&M University, January 20, 1999

"Complex Materials Synthesis: Learning from Nature", Anjou University, Suwon, Korea, February 16, 2000

"From Biogenesis to the Cooperative Assembly and Processing of Nanostructured Composite Materials", University of North Texas, February 25, 2000

"Composite Materials Synthesis: Learning from Nature", Harvard-MIT Physical Chemistry Seminar Series, April 13, 2000, and MIT Chemical Engineering Seminar, April 14, 2000

"Biosystems and Materials Synthesis", University of Pennsylvania, May 9, 2000



"Biosystems and Materials Synthesis", Philadelphia Catalysis Club, May 10, 2000

"Strategies for the Synthesis of Periodic Meso- and Macro-Porous Materials", Air Products and Chemicals, Inc., May 11, 2000

"Biosystems and Materials Synthesis", Fudan University, October 9, 2000

"Biosystems and Materials Synthesis", Jilin University, October 15, 2000

"Biosystems and Materials Synthesis", Peking University, October 16, 2000

"Mesoscale Synthesis, Structure and Function", "Light and Nanostructured Composite Materials", and "Composite Materials Synthesis: Learning from Nature", The 2000 Herbert H. Johnson Memorial Lectures, Cornell University, November 6-8, 2000

"Composite Materials Synthesis: Learning from Nature", 2001 Raymond Seidle Lecture, Indiana University, April 28, 2001

"Molecular Design and Use of 3-D Surfaces and Space", Stanford University, Department of Materials Science, April 26, 2001

"Molecular Assembly of Functional Composite Materials", California State University, Los Angeles, May 7, 2002

## CONFERENCES

### Brad Chmelka

Workshop on biomolecular Materials, San Carlos, Mexico, December, 2000.

The 2nd International Symposium on Mesoporous Molecular Sieves, Quebec, Canada, August, 2000. (keynote lecture)

International Symposium on Zeolites and Microporous Crystals, Sendai Japan, August, 2000. (keynote lecture)

Materials Research Society Symposium CC: Inorganic-Organic Composite Solids, San Francisco, April, 2000.

Materials Research Society Symposium EE: Block Copolymers, San Francisco, April, 2000.

Alpine Conference on Solid-State NMR, Chamonix, France, September, 1999.

ACS Symposium: Physical Chemistry of Sol-Gel Materials, Anaheim, CA, March, 1999.

Workshop on Advanced Materials, Jawharlal Nehru Centre for Advanced Scientific Research, Bangalore, India, November, 1998.

Workshop on "Integrating Zeolite Science and Technology," Royal Dutch Academy of Sciences, Amsterdam, The Netherlands, October, 1998.

### **Brad Chmelka's Group**

Daniel E. Favre, Dieter J. Schaefer, and Bradley F. Chmelka (conference poster). Direct Determination of Motional Correlation Times by 1D MAS and 2D Exchange NMR, 39th Experimental Nuclear Magnetic Resonance Conference, Pacific Grove, CA, March 1998.

Nick Melosh, G.D. Stucky, G.H. Fredrickson, B.F. Chmelka (submitted talk). Preparation of Mesoscopically Ordered Transparent Silica-Copolymer Monoliths and Films. American Chemical Society, Dallas, March 1998.

Sean Williams, B.F. Chmelka (contributed poster). Poly (3,4-ethylenedioxythiophene)/Poly(styrenesulfonate): Conductivity, Isotropic NMR Shift and pH Correlations. 39th Experimental NMR Conference, Asilomar, CA, March 1998.

Nick Melosh, G.D. Stucky, G.H. Fredrickson, B.F. Chmelka (submitted talk). Synthesis of Transparent Mesoscopically Ordered Silica-Block Copolymer Thin Films. International Conference on Composites Engineering (ICCE), Las Vegas, July 1998.

Daniel E. Favre, Dieter J. Schaefer, and Bradley F. Chmelka (conference talk). Intra- and Intercage Site-Hopping Dynamics of Benzene Adsorbed on Faujasite-Type Zeolites, 12th International Zeolite Conference, Baltimore, MD, July, 1998.

M.D. Mann, T.A. Zawodzinski, Electrophoretic Mobilities of Silicate and Surfactant Ions in Aqueous Solutions and Liquid Crystals, American Institute of Chemical Engineers National Meeting, Miami, November, 1998.

Sean Christiansen, M.T. Janicke, C.C. Landry, G.D. Stucky, B.F. Chmelka (submitted talk) Interfacial Structures in Mesoscopically Ordered Inorganic-Organic Composite Materials, American Institute of Chemical Engineers National Meeting, Miami, November, 1998.

Sean Christiansen (conference talk) Interfacial Structures in Mesoscopically Ordered Inorganic-Organic Materials", AIChE (American Institute of Chemical Engineers) National Conference Miami, FL, November 1998.

Nick Melosh, D. Zhao, G. Stucky, G. H. Fredrickson, B. F. Chmelka, Mesoscopically Ordered Transparent Silica-Copolymer Thin Films, presented at the ICCE International Meeting, Las Vegas, NV 1998.

Nick Melosh, D. Zhao, G. Stucky, G. H. Fredrickson, B. F. Chmelka, Preparation of Mesoscopically Ordered Transparent Silica-Copolymer Monoliths, presented at the ACS National Meeting, Dallas, TX 1998.

Nick Melosh, Labatoire de Physique des Solides, Universite Paris-Sud, Orsay, France. Nov. 20, 1998

Nick Melosh, Deparment de Chimie, Universite Paris-Jussieu, Paris, France, Nov. 24, 1998

Nick Melosh, Max Planck Institute for Polymers, Mainz, Germany. Dec. 2, 1998.

Nicholas Melosh was selected for a Graduate Student Award at the Spring, 2000 meeting of the Materials Research Society meeting. Spring, 2000.

### **Tim Deming**

American Chemical Society National Meeting, Boston, MA. Polypeptide materials Using Nickel Initiators. August, 1998

Materials And Chem. Engr. Dept., Univ. of Minnesota, MN. New Methods for Polypeptide Synthesis. June, 1998

3M Company, St. Paul, MN. New Materials Based on Polypeptides. June, 1998

American Chemical Society National Meeting, Boston, MA. Nickel Carbamate Initiators for Preparation of Functionalized Polypeptides. 8/98 (presented by Scott Curtin)

University of California, Irvine, Chemistry Department. Synthesis on polypeptide materials. January 14, 1999

Cal Tech, Chemistry and Engineering Departments. February 10, 1999.

University of Arizona, Tucson, AZ, C.S. Annual Symposium on Polymer Chemistry. April 19-22, 1999.

American Chemical Society National Meeting, Anaheim, CA. Self-assembled block copolymer composites. April, 1999.

DuPont Central Research and Development, Wilmington, NE, Polypeptide Materials. May, 1999.

Gel-Tex Pharmaceuticals, Waltham, MA. May, 1999

Bio-Environmentally Degradable Polymer Society Meeting, New Orleans, LA. Self-assembling block copolypeptides materials. August, 1999.

Synthesis of Block Copolypeptides Dupont Workshop on New Polymeric Materials, Chesapeake Farms, MD. October, 1999.

Synthesis of Polypeptides Using Transition Metal Initiators. Organic Chemistry Colloquium, Chemistry Department, UCLA. February, 2000.

Synthesis of Polypeptides Using Transition Metal Initiators Chemistry Department, North Carolina State University. March, 2000.

Self-Assembly of Block Copolypeptide Materials National Meeting of the American Chemical Society, San Francisco, CA. March 2000.

Synthesis of Polypeptides Using Transition Metal Initiators Chemistry Department. University of North Carolina. March, 2000.

Synthesis of Polypeptides Using Transition Metal Initiators Chemistry Department, University of Virginia. March, 2000.

Synthesis of Polypeptiopolypeptide Materials National Meeting of the American Chemical Society, San Francisco, CA. March 2000.

Self-Assembly of Block Copolypeptide Materials National Meeting of the American Chemical Society, San Francisco, CA. March, 2000.

Synthesis and Self-Assembly of Block Copolypeptide Materials Chemistry Department, UC Berkeley. May, 2000.

Synthesis and Self-Assembly of Block Copolypeptide Materials Polymers (East) Gordon Conference, New London, Ct. June 2000.

Synthesis and Self-Assembly of Block Copolypeptide Materials Princeton-Rhodia Block Copolymer Workshop, Princeton, NJ. June 2000.

"Functionalized Amino Acids and Their Polymers: New, Water Soluble Biocompatible Polypeptide

Synthesis and Self-Assembly of Block Copolypeptide Materials Polymers (East) Gordon Conference, New London, Ct. June, 2000.

Synthesis and Self-Assembly of Block Copolypeptide Material Princeton-Rhodia Block Copolymer Workshop, Princeton, NJ. June, 2000.

Self-Assembly of Block Copolypeptide Materials CPIMA Polymers Workshop, Stanford, CA. August, 2000.

Self-Assembly and Properties of Block Copolypeptide Materials National Meeting of the American Chemical Society, Washington DC. August, 2000.

Combinatorial Applications of Block Copolypeptides Beckman Young Investigator Workshop, Irvine CA. August, 2000.

Synthesis and Self-Assembly of Block Copolypeptide Materials Polymer Science Department, U. of Akron, OH. September, 2000.

Synthesis and Self-Assembly of Block Copolypeptide Materials ACS Polymillennial 2000 Meeting, Waiakoloa, HI. December, 2000.

Synthesis and Self-Assembly of Block Copolypeptide Materials Gordon Research Conference, Polymers (west), Ventura, CA. January, 2001.

### **Tim Deming's Group**

Jungyeon Hwang -- Oligoethyleneglycol functionalized Polyserine National Meeting of the American Chemical Society, San Francisco, CA. March 2000.

Scott Curtin -- Chain-end functionalized polypeptides National Meeting of the American Chemical Society, San Francisco, CA. March 2000.

### **Paul Hansma**

Gordon Research Conference, RI, "Nanostructure Fabrication", 1998

American Physical Society, March Meeting, Los Angeles, CA, Division of Biological Physics, 1998

Arizona State University, Site Visit, Department of Biophysics, "Biomineralization: how do Abalone Shells Grow? New Insights from Scanning Probe Microscopy", in VSEE/CSSS/CSSER Nanoscience and Technology minisymposium, INVSEE External Advisory Board Meeting and Visit to the Stuart Lindsay Laboratory involved with cryo-AFM and MAC Mode, 1998

American Chemical Society National Meeting, "Symposium on Microscopy Techniques in Bio-Interfacial Science", Boston, MA, 1998

First International Conference on Scanning Probe Microscopy of Polymers, at UCSB, August 27-29, (1999).

Programme NSR-RIM Symposium, Conference Centre 'Woudschoten', Zeit in the Netherlands, January 13 and 14, 1999. Invited talk: "Architecture & Function of Fracture-Resistant, Biological Materials", on January 14, 1999.

Invited Talk "A Secret from the Sea" at a workshop on "Single Molecule Biochemistry" at the University of Leiden, January 21, 1999.

Invited Seminar , "Mechanical Measurement on Single Molecules" at Mayo Clinic, September 24, 1999.

### **Paul Hansma's Group:**

Symposium Presentation, American Physical Society, Los Angeles, March, ("Study of Proteins with a High-Sensitivity Atomic Force Microscope.") by T.S. Schaffer, M.B. Viani, B.L. Smith, A.M. Belcher, H.E. Gaub, G.D. Stucky, D.E. Morse and P.K. Hansma; presented by T.S. Schaffer. 1998.

Tilman Schäffer (invited talk). Abalone Shell as a High-Performance Microlaminate Material, University of California Educational Outreach Program. UCSB, February 1998.

Bettye L. Smith (invited talk). Using the Atomic Force Microscope to Understand Nature's Composite Materials. University of California Educational Outreach Program. UCSB, February 1998.

B. L. Smith. Using the Atomic Force Microscope to Understand Nature's Composite Materials University of California Educational Outreach Program, Santa Barbara CA. February 1998

Mario B. Viani, T.E. Schäffer, A. Chand, B.L. Smith, and P.K. Hansma. Small cantilevers for atomic force microscopy and force spectroscopy of biological molecules. American Physical Society, Los Angeles, CA, March 1998.

Tilman Schäffer. Study of Proteins with a High-Sensitivity Atomic Force Microscope. American Physical Society, Los Angeles, CA, March 1998.

Tilman Schäffer (invited talk). Biomineralization of Abalone Shell Nacre Investigated with Scanning Probe Microscopy, Raychem Corp., Menlo Park, CA, April 1998.

B. L. Smith and M. C. MacLeod. A novel approach for analyzing the structure of DNA modified by benzo[a]pyrene diol epoxide at single molecule resolution. American Association for Cancer Research, New Orleans, Louisiana. 28 March-1 April 1998

Tilman Schäffer (invited talk). Study of Biological Systems with New Scanning Probe Microscopes. Indiana University, Physics Department, Bloomington, IN, May 1998.

Tilman Schäffer (invited talk). New Atomic Force Microscopes and Small Cantilevers. Digital Instruments, Inc., Santa Barbara, CA, June 1998

Tilman Schäffer (invited talk). Investigation of Biological Systems with New Scanning Probe Microscopes. Max Planck Institute for Biophysical Chemistry, Göttingen, Germany, June 1998.

Bettye L. Smith (invited talk). Can Marine Organisms control Crystal Growth with Proteins? American Chemical Society Symposium on Microscopy Techniques in Bio-interfacial Science, Boston, MA, August 1998

Bettye L. Smith (invited talk). Keeping Pace with Nanotechnology: Novel Applications for Atomic Force Microscopy. Molecular Nanotechnology Conference, San Francisco, CA, December 1998

B. L. Smith. Keeping pace with nanotechnology: Novel Applications for Atomic Force Microscopy. International Business Communications Conference, 7-8 December 1998

Gebeshuber I.C., Kindt J.H., Thompson J.B., DeAmo Y., Brzezinski M., Stucky G.D., Morse D.E. and Hansma P.K. "Atomic force microscopy of diatoms in vivo", in: Abstracts of the 15th

North American Diatom Symposium, Pingree Park Campus, Colorado State University, September 1999, p. 8. (15th North American Diatom Symposium, Pingree Park Campus, Colorado State University) (1999)

B. L. Smith. The Behavior of active biopolymers on functionalized surfaces. Clinical Microsensors (invited talk); Pasadena CA. March 1999

B. L. Smith, G. Palocz, and R. Paul Levine. Discerning Nature's Mechanism For Making Complex Biocomposite Crystals. The 11th American Conference on Crystal Growth and Epitaxy, August 1999, Tucson, Arizona

B. L. Smith, T. E. Schäffer, M. Viani, J. B. Thompson, N. A. Frederick, J. Kindt, A. Belcher, G. D. Stucky, D. E. Morse, and P. K. Hansma. Molecular mechanistic origin of the toughness of natural adhesives, fibers, and composites. 1st International Conference on Scanning Probe Microscopy of Polymers, Santa Barbara, CA. 27-29 August 1999

Gebeshuber I.C., Kindt J.H., Thompson J.B., DelAmo Y., Stachelberger H., Brzezinski M., Stucky G.D., Morse D.E. and Hansma P.K. (2000) "Adhesives made by benthic diatoms studied by in vivo Atomic Force Microscopy", *Biophys. J.*, in press is accepted for the 44th Annual Meeting of the Biophysical Society, February 12-16, 2000, New Orleans, Louisiana.

### **Daniel Morse**

Lecture, Howard Hughes Medical Institute Undergraduate Research Colloquium, University of California, Santa Barbara, ("Biom mineralization and Bio-Chips: Research and Career Opportunities Where the Biotechnology and Optoelectronic Revolutions Meet.") January, 1998.

Invited Lecture, University of Paris, Paris, France, CNRS Visiting Lectureship. ("Biological and Biomimetic Nanofabrication with Calcium and Silicon.") March, 1998.

Plenary Opening Symposium Presentation (Invited), 4th International Munich Silicon Days Symposium, Munich, Germany,. ("Silicon Biotechnology: Proteins, Genes and Molecular Mechanisms Controlling Biological Nanofabrication with Silicon") April, 1998

Invited Lecture. Los Alamos National Laboratory, Los Alamos, NM, ("Biom mineralization: Molecular Mechanisms of Biological Nanofabrication with Calcium and Silicon.") April, 1998.

Invited Symposium Overview, as Chairman, Opening Session, Gordon Conference on Biom mineralization, Henniker, NH, ("Interfacial Interactions Controlling Biom mineralization.") August, 1998.

Invited Symposium Presentation, Gordon Conference on Biom mineralization, Henniker, NH, ("The Biosilica World: Proteins, Genes and Molecular Mechanisms Controlling Biological Nanofabrication with Silicon.") August, 1998.

Invited Symposium Presentation, U.S.-India Joint Materials Research Symposium, Bangalore, India, ("Biom mineralization: Molecular Mechanisms of Biological Nanofabrication with Calcium and Silicon.") November, 1998.

Seminar, Department of Molecular Cellular and Developmental Biology, University of California, Santa Barbara, (Silicon Biotechnology: Cloning at the Interface Where Two Worlds Meet.") November, 1998.

Invited Presentation, Emerging Technologies Series, U.S. Dept. of Defense, Washington, D.C., ("Biomolecular and Biomimetic Nanofabrication with Calcium and Silicon.") January, 1999.

Invited Symposium Presentation, International Symposium on Calcified Tissues, Eilat, Israel, ("Molecular Mechanisms Governing Nanofabrication and Properties of Gastropod Pearl and Shell.") February, 1999

Invited Symposium Presentation, U.S.-Korea-Australia Advanced materials Research Workshop, Korean Advanced Institute for Science and Technology, Australian Central Scientific and Industrial Research Organization and UCSB Materials Research Laboratory, University of California, Santa Barbara, ("Biomolecular and Biomimetic Nanofabrication with Silicon.") February, 1999

Invited Plenary Presentation, 32nd Organosilicon Symposium, Milwaukee, ("Silicon Biotechnology: Genes and Proteins Controlling Biosilica Nanofabrication Suggest New Routes for Synthesis of Silica and Silsesquioxanes.") March, 1999

Invited Symposium Presentation, U.S.-France Joint Materials Research Symposium, Nantes, France, ("Biom mineralization: Molecular Mechanisms of Biological Nanofabrication with Calcium and Silicon.") March, 1999.

Invited Keynote Symposium Presentation, Frontiers in Materials Research Symposium, Materials Research Society, San Francisco, ("Silicon Biotechnology: Genes and Proteins Controlling Biological Nanofabrication with Silica.") April, 1999

Invited Presentation, U.S. Congressional Staff-California Healthcare Industrial Institute, University of California, Santa Barbara, ("From Biology to Biochips: Advanced Materials for the 21st Century from Biom mineralization.") April, 1999.

Invited Symposium Presentation, 12th International Symposium on Organosilicon Chemistry, Sendai, Japan, ("Silicon Biotechnology: Harnessing the Genes and Proteins that Control Biological Nanofabrication with Silicon to Make Silsesquioxanes.") May, 1999

Invited Seminar, Naval Research Laboratory, Washington, D.C., ("Biomolecular and Biomimetic Nanofabrication with Calcium, Transition Metals, Rare Earths and Silicon.") May, 1999.



Invited Keynote Address, DFG Symposium on Special Topics in Silicon Chemistry, Bielefeld, Germany. ("Catalytic and Templating Control of Polysiloxane Synthesis by Native, Genetically Engineered and Biomimetic Proteins.") May, 1999

Invited Seminar, University of Washington Nanotechnology Center, Seattle, ("Silicon Biotechnology: Harnessing the Genes and Proteins Controlling Biosilica Nanofabrication for New Routes to Synthesis of Silica and Organosilicon-based Composites.") June, 1999.

Invited Presentation, Workshop on the Enzymatic Synthesis of Organosilicon Compounds, University of California, Santa Barbara, ("Molecular Biological and Biomimetic Synthesis of Silica and Silsesquioxanes.") August, 1999.

Seminar, Department of Molecular Cellular and Developmental Biology, University of California, Santa Barbara,. ("Silicon Biotechnology") September, 1999

Seminar, Genencor International Corporation, Palo Alto, California,. ("Silicon Biotechnology Proteins, Genes and Molecular Mechanisms Controlling Biological Nanofabrication with Silicon".) October, 1999

Invited Symposium Presentation, Biotechnology Leadership Summit, Cottage Hospital, Santa Barbara, ("Biomolecular Materials") October, 1999.

Invited Presentation, Trustees Meeting, University of California, Santa Barbara, ("From Biology to Bio-Chips: Advanced Materials for the 21st Century.") October, 1999.

Seminar, Procter and Gamble Corporation, Cincinnati,. ("Silicon Biotechnology Offers New Routes for Synthesis of Structure-Controlled Silica and Silsesquioxanes.") November, 1999

Invited Keynote Presentation, 33rd Organosilicon Symposium, Midland, MI,. ("Biomolecular and Biomimetic Nanofabrication with Silicon.") April, 2000

Invited Presentation, Gordon Research Conference on Biomineralization, New Hampshire,. ("Harnessing the Proteins and Molecular Mechanisms Controlling Biomineralization with Calcium and Silicon.") August, 2000

Nanoscale control of biomineralization in abalone, sponge and diatoms, Invited poster, American Geophysical Society Meeting, December 2000.

Invited Lecture, "High-Performance Nanostructured Biomaterials: The Secret is in the Synthesis" Ceramics Society Annual Symposium, Cocoa Beach, FL 1/01

Invited Lecture, "High-Performance Nanostructured Biomaterials and Biomimetics: The Secret is in the Synthesis" NASA Biotechnology, Smart Materials and Nanotechnology Forum, Hampton, VA 1/01

Invited Lecture, "Smart, Nanostructured Biomaterials: The Secret is in the Synthesis" Society for Photonic and Industrial Electronic Engineering Symposium, Newport Beach, CA 3/01

Invited Lecture, "High-Performance Nanostructured Biomaterials: The Secret is in the Synthesis" MIT - BioEngineering Program & Dept. of Chemistry, Cambridge, MA 3/01

Keynote Lecture, "High-Performance Nanostructured Biominerals: The Secret is in the Synthesis" Biomineralization Symposium, International Biomaterials Conference, Minneapolis, MN 4/01

Invited Lecture, "High-Performance Nanostructured Composites: The Challenge is in the Synthesis" IBM Corp. "Grand Challenges in Nanotechnology Program," IBM Research Center, Almaden, CA 4/01

Invited Lecture, "Optoelectronic Applications Of The Intimate Coupling Of Proteins And Dna With Silicon-Based Materials" Materials Research Society Symposium International Symposium, (Biomolecular Electronics Symp.), San Francisco, CA 4/01

Invited Lecture, "High-Performance Nanostructured Biomaterials: The Secret is in the Synthesis" UOP Corporation, "Frontiers Program", Arlington Heights, IL 5/01

Invited Presentation, "Silicon Biotechnology Offers New Routes to Materials Synthesis" Third World Academy of Science-MRL Colloquium, Trieste, Italy 5/01

Invited Lecture, "Silicon Biotechnology: New Routes for Structure-Directing Catalysis of Polysiloxane Synthesis" International Symposium on "Catalysis by Design", Amsterdam, Holland 5/01

Invited Seminar, "Silicon Biotechnology Reveals New Routes to Nanostructured Materials" University of Zurich, Dept. of Chemistry, Zurich 6/01

Invited Lecture, "Proteins, Genes and Biomolecular Mechanisms Controlling Biological Nanofabrication Offer New Routes to High-performance Materials" National Research Council Workshop on "Challenges for the Chemical Sciences in the 21st Century-Materials and Manufacturing," Washington, DC 6/01

Invited Seminar, "Proteins, Genes and Molecular Mechanisms Controlling Biological Nanofabrication with Calcium and Silicon Offer New Routes to Hierarchically Organized, Functional Composites" Calif. NanoSystems Institute, UCSB 7/01

Invited Lecture, "From Sponges to Silicon Biotechnology: Mechanisms of Biomineralization Reveal New Routes to High-Performance Materials" International Symposium on Self-Assembling Peptides, Heraklion, Crete 7/01

Invited Lecture, "Proteins, Genes and Molecular Mechanisms Controlling Biomineralization with Calcium and Silicon Offer New Routes to Nanostructured Materials" Genetics Institute, Larnaka, Cyprus 7/01

Invited Lecture, "Silicon Biotechnology: Harnessing Structure-Directed Siloxane Polymerization" International Symposium on "BioTransformation 2001", Darmstadt, Germany 8/01

Invited Lecture, "Silicon Biotechnology and its Extensions: Harnessing Structure-Directing Polymerization" Honeywell Corp., Morristown, NJ 10/01

Invited Lecture, "Silicon Biotechnology and its Extensions: Harnessing Structure-Directing Polymerization" DuPont Corp. Central Research & Development Wilmington, DE 10/01

Invited Lecture, "Mechanisms of Biomineralization with Calcium and Silicon Reveal New Routes to Hierarchically Organized Composite Materials" Materials Research Society International Symposium (Symp. on "BioInspired Materials"), Boston, MA 11/01

Invited Lecture, "Silicon Biotechnology: Proteins, Genes and Biomolecular Mechanisms Open New Routes to Nanofabrication of High-Performance Silicon-based Materials" DOE Workshop on Biomolecular Materials, San Diego, CA 1/02

Invited Lecture, "Surprises and Payoffs from Biomineralization: Unanticipated Mechanisms of Biological Nanofabrication with Calcium and Silicon Offer New Routes to Biomimetic Synthesis" University of Virginia, Dept. of Chemistry, Charlottesville, VA 2/02

Invited Presentation, "New Approach to DNA and RNA Biosensors" Materials Research Laboratory (MRL) Industrial Outreach Symposium, UCSB 2/02

Invited Presentation, "Biotechnology Provides New Routes to Structure-Directed Synthesis of Polysiloxanes and Metallo-oxanes" CNRS-UCSB Workshop, CNRS, Paris 4/02

Invited Lecture, "Silicon Biotechnology Offers New Paths for Structure-Directing Polymerization of Silica and Silsesquioxanes" Materials Research Society International Symposium, San Francisco, CA 4/02

Invited Lecture, "Biotechnology Provides New Routes to nanostructure-Directing Polycondensation of Silica, Silsesquioxanes and Metallo-oxanes" Dow Chemical Corp. Central Research & Development, Midland, MI 5/02

Site-visit presentation: UCSB's Ecotechnology Project Impact, Significance and Administration" Site visit by W.M. Keck Foundation for successful proposal for \$1.5M for a new interdisciplinary program, UCSB 5/02

Invited Public Lecture, "The Hidden Beauty of Pearls: Nature's Blueprints for High-Performance Materials" Rotary Club, Goleta, CA 5/02

Invited Lecture, "Silicon and Metal Oxide Biotechnology: New Routes to Catalytic Nanofabrication of High-Performance Materials" International Electronic Materials Conf., UCSB 6/02

Invited Lecture, "DNA Photophysics: DNA-based Sensors and Photoconductivity" DuPont Corp. Central Research & Development, Wilmington, DE 7/02

Invited Lecture, "Inorganics and Organometallics: Biotechnology and Biomimetics Provide New Routes to Structure-Directing, Catalytic Nanofabrication" DuPont Corp. Central Research & Development, Wilmington, DE 7/02

Contributed Lecture, "Biotechnology Provides New Routes to Nanofabrication of High-Performance Organometallics International Symposium on Organometallic Chemistry, Corfu 7/02

Invited Lecture, "Biomolecular and Biomimetic High-Performance Nanocomposites" NASA Institute for Computational Analysis, Science and Engineering 50th Anniversary Symposium, Newport News, VA 7/02

Keynote Lecture, "Silicon Biotechnology: The Vision Becomes a Reality" XIII International Organosilicon Symposium, Guanajuato, Mexico 8/02

Contributed Presentation, "Silicon Biotechnology and the World of Future Opportunities in Biomolecular Engineering" Molecular, Cellular & Developmental Biology/Biomolecular Science & Engineering Research Retreat, UCSB 9/02

Invited Lecture, "Silicon Biotechnology: Proteins, Genes and Biomolecular Mechanisms Open New Routes to Nanofabrication of High-Performance Silicon-based Materials" DOE Workshop on Biomolecular Materials, San Diego, CA 1/02

Invited Lecture, "Surprises and Payoffs from Biomineralization: Unanticipated Mechanisms of Biological Nanofabrication with Calcium and Silicon Offer New Routes to Biomimetic Synthesis" University of Virginia, Dept. of Chemistry, Charlottesville, VA 2/02

Invited Presentation, "New Approach to DNA and RNA Biosensors" Materials Research Laboratory (MRL) Industrial Outreach Symposium, UCSB 2/02

Invited Presentation, "Biotechnology Provides New Routes to Structure-Directed Synthesis of Polysiloxanes and Metallo-oxanes" CNRS-UCSB Workshop, CNRS, Paris 4/02

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Invited Lecture, "Inorganics and Organometallics: Biotechnology and Biomimetics Provide New Routes to Structure-Directing, Catalytic Nanofabrication" DuPont Corp. Central Research & Development, Wilmington, DE 7/02

Contributed Lecture, "Biotechnology Provides New Routes to Nanofabrication of High-Performance Organometallics International Symposium on Organometallic Chemistry, Corfu 7/02

Invited Lecture, "Biomolecular and Biomimetic High-Performance Nanocomposites" NASA Institute for Computational Analysis, Science and Engineering 50th Anniversary Symposium, Newport News, VA 7/02

Keynote Lecture, "Silicon Biotechnology: The Vision Becomes a Reality" XIII International Organosilicon Symposium, Guanajuato, Mexico 8/02

Contributed Presentation, "Silicon Biotechnology and the World of Future Opportunities in Biomolecular Engineering" Molecular, Cellular & Developmental Biology/Biomolecular Science & Engineering Research Retreat, UCSB 9/02

### **Galen Stucky**

"Mesoporous Materials and Biomaterials", US Department of Energy Council on Chemical Sciences Workshop on Partially Ordered Chemical Systems, Santa Fe NM, May 10-14, 1998

"Periodic Cage and Porous (2 to 40 nm) Silica Structures: Synthesis, Thin Film Processing, and Dielectric Properties", Symposium on Hybrid Materials, Materials Research Society 1998 Spring Meeting, San Francisco CA, April 13-17, 1998

"Using Interfaces, Non-equilibrium, and Multiprocesses in the Molecular Design and Synthesis of Materials", Symposium on Low-Dielectric-Constant Materials and Applications in Microelectronics IV, Materials Research Society 1998 Spring Meeting, San Francisco CA, April 13-17, 1998

"Using Interfaces, Non-Equilibria, and Multiprocesses in the Molecular Design of Silica Materials from Ångströms to Centimeters", IVth Münchner Silicontage, Munich, Germany, April 6-9, 1998

"Using Interfaces, Non-equilibrium and Multiprocesses for the Molecular Design of Materials from Å to cm", Stanford University Hopkins Marine Station, May 21, 1998

"Using Interfaces, Spatially Competing Domains, and Multiprocesses in the Molecular Design of Composite Materials", Air Products and Chemicals, Inc., Allentown PA, June 10, 1998

"Using Interfaces, Spatially Competing Domains, and Multiprocesses in the Molecular Design of Composite Materials", Lucent Technologies, Murray Hill NJ, June 9, 1998

"Using the Organic-Inorganic Interface to Uniquely Define Pore and Macroscale Structure", International Symposium on Mesoporous Molecular Sieves, Baltimore MD, July 10-12, 1998

"Periodic (1 to 50 nm) Porous Silica Synthesis", Institut de Chimie des Surfaces et Interfaces (ICSI-CNRS) Conference "Silica from Synthesis to Application", Mulhouse, France, September 1-4, 1998

"Using Interfaces, Spatially Competing Domains And MultiProcesses in the Molecular Design Of Composite Materials", First International Conference on Inorganic Materials: Synthesis, Characterization, Properties and Applications of Inorganic Materials, Versailles, France, September 16-19, 1998

"Domain Separation with Emulsions and Polymers in the Synthesis of Organic/Inorganic Hybrid Materials", UCSB-JNCASR-IISC Workshop on Frontiers of Materials Science and Engineering, Bangalore, November 15-20, 1998

"Using Interfaces, Spatially Competing Domains And MultiProcesses in the Molecular Design Of Composite Materials", 50th ACS Southeast Regional Meeting, North Carolina, November 4-7, 1998

"Silicon, Germanium, and Tin Clathrate Cage Structures as Thermoelectric Materials", Symposium on Thermoelectric Materials: The Next Generation Materials for Small-Scale Refrigeration and Power Generation Applications, Materials Research Society 1998 Fall Meeting, Boston, November 30-December 4, 1998

"Using Competing Processes, Spatial Domains, and Interfaces in the Assembly of Composite Materials", IC'99 (Joint meeting of Inorganic Division of Royal Australian Chemical Institute and Inorganic Specialist Group of The New Zealand Institute of Chemistry), Wellington, New Zealand, January 31-February 4, 1999

"Spatio-temporal Considerations in Composite Materials Synthesis", KAIST/UCSB-MRL/CSIRO Workshop on Advanced Materials, February 21-24, 1999

"Mesoporous Zeolites", DSRC Study on Nanostructured Materials and Technologies, Arlington VA, March 16-17, 1999

"Hierarchically Ordered Silica-Organic Composites and Porous Oxides", FIAP Symposium on Physics of the Silicon Bond, Centennial APS Meeting, Atlanta, March 20-26, 1999

"The Biogenesis and Cooperative Assembly of Complex Materials", Symposium on Physical Chemistry and Sol-Gel Materials, 213th National ACS Meeting, Anaheim, March 21-25, 1999

"Molecular Design of Porous Materials", Florida Catalysis Conference, Palm Coast FL, April 19-23, 1999

"Using Interfaces and Competing Assembly Processes in the Molecular Design and Synthesis of Nanostructured Materials", Workshop on Nanostructured Materials, University of Massachusetts, Amherst, May 12, 1999

"Using Interfaces and Competing Assembly Processes in the Molecular Design and Synthesis of Composite Materials", International Conference on Rational Approaches to New Materials Design and Synthesis, Philadelphia, May 20-21, 1999

"Multiphase Synthesis and Hierarchical Structures", Gordon Research Conference on Zeolitic and Structured Materials, Plymouth NH, June 13-19, 1999

"Silicon Functionalization in High-Surface-Area Silicas", Colloquium on Enzymatic Alkylation of Silicon (sponsored by Dow Corning Corporation), University of California, Santa Barbara, August 12-14, 1999

"The Biogenesis and Cooperative Assembly of Complex Materials: (1) Learning from Nature; (2) Single System Synthesis and Processing in the Laboratory", NTU-UCSB Workshop on Nanostructured Composite Materials., National Taiwan University, Taipei, September 16-17, 1999

"Synthesis Paradigms for the Creation of Easily Processible Metal Oxide Composite Materials", Keynote Speaker, Sol-Gel '99 (10th International Workshop on Glasses, Ceramics, Hybrids, and Nanocomposites from Gels), Yokohama, Japan, September 19-24, 1999

"Using Molecular Biology and Chemistry to Create Complex Materials and Opto-electronic Arrays", 1999 Industrial Physics Forum (Annual Meeting of the Corporate Associates of the American Institute of Physics), Annandale NJ, October 24-26, 1999

"Molecular Design, Synthesis, Processing, and Use of 3-d Surfaces and Space in Nanostructured Composite Materials", ARO Workshop on Templated Nanoscale Synthesis and Reactivity, Rodman Center, Army Research Laboratory, October 20-21, 1999

"Nanocomponent Assembly via Single-System Processing and 3-D Patterning on Multiple Length Scales", SRC/NASA Workshop on Self Assembly for Nanoelectronics, NASA Ames Research Center, November 15-17, 1999

"Mesostructured Silica Optical Devices", Symposium on Micro- and Nano-Photonic Materials and Devices, Optoelectronics 2000 at Photonics West (SPIE meeting, San Jose), January 27-28, 2000

“Biomimetics and Bio-inspired Materials”, National Forum on Materials and Processing, National Materials Advisory Board, Washington, D. C., February 8-9, 2000

“From Biogenesis to the Cooperative Assembly and Processing of Nanostructured Composite Materials”, First International Symposium on Hyperstructured Organic Materials, Seoul, February 17, 2000

“Light and Nanostructured Composite Materials”, Korea Institute of Science and Technology, Seoul, February 19, 2000

“Nanocomposite Definition by Bio and Benchtop Polymers”, Symposium on Polymeric Materials: Science and Engineering, American Chemical Society National Meeting, San Francisco, March 26-31, 2000

“From Biogenesis to the Cooperative Assembly and Processing of Nanostructured Composite Materials”, International Workshop on Advances in Materials Science and Technology, Institute of Material Research and Engineering (IMRE), National University of Singapore, April 3-6, 2000

“Nanocomposite Definition by Bio and Benchtop Polymers”, DuPont Horizons in Biotechnology Forum, Wilmington DE, May 8, 2000

“From Biogenesis to the Cooperative Assembly and Processing of Nanostructured Composite Materials”, Symposium in celebration of the 100th anniversary of the founding of the Chemical Institutes at Hessische Straße, Berlin, June 14, 2000

“Multiphase Assembly of Nanoscale Materials”, EMSL 2000 Nanoscience and Nanotechnology Symposium, Pacific Northwest National Laboratory, June 21-23, 2000

“Synthesis and Processing of Nanocomposites: From Porous Materials to Optical Breadboards and Low Dielectrics”, Second International Symposium on Mesoporous Molecular Sieves (ISMMS 2000), Quebec, August 27-September 2, 2000

“Organizing Domains in Composite Materials: Synthesis, Structure and Function”, ICTP/UCSB/TWAS Workshop on Frontiers in Materials Science, Trieste, May 15-18, 2001

“Biosystems and Materials Synthesis”, EPFL/ETHZ/UCSB/WIS Workshop on Advanced Materials, Crêt-Bérard, Switzerland, 9-13 September 2001

“Organizing Domains and Interfaces in Composite Materials: Synthesis, Structure and Function”, American Chemical Society Regional Meeting, Santa Barbara CA, October 29-30, 2001

“Functional Inorganic Materials Templated by Organic Self Assembly”, Materials Research Outreach Symposium, UC Santa Barbara, February 6-8, 2002



“Assembly of Interactive Functional Units and Domains in 3-D Composite Systems During Synthesis and Processing”, Symposium on Functional Nanostructured Materials through Multiscale Assembly and Novel Patterning Techniques, Materials Research Society Spring Meeting, San Francisco, April 2-5, 2002

“Molecular Assembly of Organized Composites”, Award Lecture, Division of Inorganic Chemistry, American Chemical Society National Meeting, April 7-11, 2002 “Organizing System Component Domains in Composite Materials”, 37th ESF/EUCHEM Stereochemistry Conference, Bürgenstock (Switzerland), April 13-19, 2002

“Organizing Domains and Interfaces in Composite Materials: Synthesis, Structure, and Function”, 3rd International Symposium on Mesosstructured Materials, Jeju (Korea), July 8-11, 2002

### **Dan Morse's & Galen Stucky's Groups**

Peidong Yang, Mesoporous metal oxides: synthesis, structures and properties, Gordon Research Conference: Solid State Chemistry, New London, NH, July, 1998.

Peidong Yang (invited talk), Block copolymer templating synthesis of mesoporous metal oxides with large ordering lengths and semicrystalline walls. American Chemical Society National Meeting, Boston, MA, Aug., 1998.

Angela Belcher (invited talk) National User Fabrication Network Symposium, Patterning in Nature, Santa Barbara, 1998.

Angela Belcher (invited seminar) First Steps in Harnessing the Mechanisms of Nanofabrication of the Microlaminate Composite of Molluscan Nacre. Department of Chemistry, University of Texas at Austin. Austin 1998.

Peidong Yang (invited talk), Generalized syntheses of large-pore mesoporous metal oxides with nanocrystalline frameworks, Lucent Technologies, Bell Laboratories, Murray Hill, NJ, Sept., 1998.

Ulrike Ciesla (invited poster). Interaction of Serine, Ser-Ser, and Poly-Serine with Silicic Acid. Deutsche Festkoerpertagung, Saarbruecken, Germany, September 1998.

Katsuhiko Shimizu (invited talk) Molecular mechanism of biomineralization with silicon. Japanese Materials Research Society Symposium, Kawasaki, Japan, December 11, 1998.

Katsuhiko Shimizu (invited talk) Molecular biology of sponge biosilica. Biomineralization Symposium, Tokyo, Japan, December 14, 1998.

Invited Symposium Presentation, Materials Research Symposium (Nanofabrication Symposium), Boston, MA, November, 1998. (“Nanoparticle Self-Assembly Using Hybrid Biomolecules.”) by A.M. Belcher, D. Margolese, D. Bebinger, D. E. Morse, G.D. Stucky and E. Hu; presented by A.M. Belcher.

Poster Presentation, U.S.-Korea-Australia Advanced materials Research Workshop, Korean Advanced Institute for Science and Technology, Australian Central Scientific and Industrial Research Organization and UCSB Materials Research Laboratory, University of California, Santa Barbara, February, 1999. ("Proteins from Nacre Control Crystal Growth.") by M. Michenfelder, K. Le, F. Coblenz, B. Smith, J. Thompson, G. Paloczi, G. Stucky, P. Hansma and D. Morse; presented by M. Michenfelder.

Poster Presentation, U.S.-Korea-Australia Advanced materials Research Workshop, Korean Advanced Institute for Science and Technology, Australian Central Scientific and Industrial Research Organization and UCSB Materials Research Laboratory, University of California, Santa Barbara, February, 1999. ("Silicon Biotechnology Reveals New Routes to Materials.") by K. Shimizu, J. Cha, Y. Zhou, C. Lawrence, S. Christiansen, B. Chmelka, T. Deming, G. Stucky and D. Morse; presented by K. Shimizu.)

Symposium Presentation, American Chemical Society Symposium, Anaheim, March, 1999. "Molecular Mechanisms of Biomineralization with Silicon." by K. Shimizu, J. Cha, Y. Zhou, G.D. Stucky and D. E. Morse; presented by K. Shimizu.

Invited Symposium Presentation, American Conference on Crystal Growth and Epitaxy, Tucson, August, 1999. ("Molecular Mechanisms Governing Nanofabrication and Properties of Abalone Shell.") by M. Michenfelder, B. Smith, J. Thompson, G. Paloczi, A. Belcher, G. Stucky, P. Hansma and D. Morse; presented by M. Michenfelder.

Invited Symposium Presentation, 2nd International Lake Louise Conference on Composites, Lake Louise, Canada, November, 1999. ("Silicon Biotechnology Reveals New Routes to Materials.") by J. Cha, K. Shimizu, Y. Zhou, C. Lawrence, S. Christiansen, B. Chmelka, T. Deming, G. Stucky and D. Morse; presented by J. Cha.

Invited Symposium Presentation, Materials Research Society Annual Meeting, Boston, December, 1999. ("Biological and Biomimetic Synthesis of Silicas and Silsesquioxanes.") by J. Cha, K. Shimizu, Y. Zhou, C. Lawrence, S. Christiansen, B. Chmelka, T. Deming, G. Stucky and D. Morse; presented by J. Cha.

Poster Presentation, "Biomolecular and Biomimetic Nanofabrication of Silica and Silsesquioxane-based Materials, by J. Cha, J. Harreld, K. Shimizu, G. Stucky, T. Deming and D. Morse; presented by Jennifer Cha 2/00

Materials Research Laboratory Industrial Outreach Program, UCSB Poster Presentation, "Mechanisms Governing the Biofabrication of Highly Ordered Nanocomposites by Purified Molluscan Shell Proteins", M. Michenfelder, J. Weaver, C. Lawrence, K. Le and D. Morse; presented by M. Michenfelder 2/00

Materials Research Laboratory Industrial Outreach Program, UCSB Invited Lecture, "Nano-patterned Arrays for Protein Binding to Silicon-Based Materials Using Soft Lithography," by J. Gaul, J. Sumerel, Y. Zhou and D. Morse; presented by John Gaul. 4/00

33rd Organosilicon Symposium, Midland, MI Invited Lecture, "Biosilicification in Sponges and its Application for In Vitro Synthesis of Polysiloxanes, by K. Shimizu and D. Morse; presented by Katsuhiko Shimizu 6/00

International Congress on In Vitro Biology, San Diego, CA Invited Lecture, "Biomolecular and Biomimetic Mechanisms Controlling Nanostructure-Directed Synthesis of Silica and Silsesquioxanes, by J. Cha, Y. Zhou, J. Cao, K. Shimizu, G. Stucky and D. Morse; presented by Jennifer Cha. 10/00

IX International Congress on Experimental Mechanics, (Biologically Inspired Materials Symposium), Minneapolis, MN Invited Lecture, "Biomolecular and Biomimetic Mechanisms Controlling Nanostructure-Directed Synthesis of Silica and Silsesquioxanes, by J. Cha, Y. Zhou, J. Cao, K. Shimizu, G. Stucky and D. Morse; presented by Jennifer Cha. 12/00

International Chemical Symposium, (Biomineralization Symp.). Pacific Rim Chemical Societies, Honolulu, HI Invited Poster, "Nanoscale Control of Biomineralization in the Abalone, Sponge and Diatom, by M. Brzezinski, D. Morse, P. Hansma, and B. Chmelka; presented by Mark Brzezinski 12/00

International Symposium, American Society of Limnology and Oceanography, San Francisco, CA Poster, "Biomolecular Polymers and Mechanisms Yield New Methods for Shape-Controlled Synthesis of Patterned Silicon-based Materials," by J. Cao, J. Gaul, M. Merget, J. Sumerel, J. Weaver, Y. Zhou and D. Morse; presented by Jixiang Cao. 1/01

Materials Research Laboratory Industrial Outreach Program, UCSB Poster, "Development of Aligned DNA Complex Thin Films for Photonic and Electronic Applications," by W. Yang, C-Y Yanag, D. Moses, AJ Heeger and DE Morse; presented by Wenjun Yang 2/02

Materials Research Laboratory Industrial Outreach Program, UCSB Poster, "Bone Indentation Recovery Time Correlates with Bond Reforming Time," by J Thompson, J. Kindt, B. Drake, H. Hansma, D. Morse and P. Hansma; presented by George Thompson. 2/02

Materials Research Laboratory Industrial Outreach Program, UCSB Poster, "Highly Ordered Substrate-Directed Silica Deposition in 3-Dimensional Space," by J. Weaver, L. Pietrasanta, J. Cha, K. Shimizu, Y. Zhou, P. Hansma, G. Stucky, and D. Morse; presented by James Weaver. 2/02

Materials Research Laboratory Industrial Outreach Program, UCSB Poster, "Organization of Calcium Carbonate on a Multi-Dimensional Length Scale," by L. Euliss, J. Cha, D. Morse, T. Deming and G. Stucky; presented by Laurie Euliss. 2/02

Materials Research Laboratory Industrial Outreach Program, UCSB Invited Oral and Poster Presentation, "Genetic Construction of a Chimeric Silicatein-Red Fluorescent Protein", presented by Sara Alvarez 5/02

National Nanofabrication Users' Network Research Meeting of Undergraduate Fellowship Winners; Howard University

Invited Presentation, "Molecular Mechanisms Governing Nanofabrication and Properties of Abalone Nacre," by G. Fu, M. Michenfelder, J. Thompson, G. Falini, A. Belcher and D. Morse; presented by Germaine Fu. 5/02

International Symposium on Biomimetic Engineering, Orlando, FL Poster, "DNA Alignment and Characterization," by CY Yang, WJ Yang, D. Moses, D. Morse, and AJ Heeger; presented by Cui Ying Yang. 7/02

International Conference on Synthetic Metals, Shanghai Invited Oral Presentation (and Poster), "Soluble Nacre Proteins that Govern the Calcite-to-Aragonite Transition in Abalone Shell", by G. Fu, S. Valiyaveetil and D.E. Morse; presented by Germaine Fu 8/02

Gordon Research Conference on Biomineralization, Hanover, NH Invited Poster, "Novel Approaches for Investigating Silica Spicule Biosynthesis in Living Demosponges," by J. Weaver, K. Shimizu, J. Cha, P.K. Hansma, G. Stucky and D. Morse; presented by James Weaver 8/02

Gordon Research Conference on Biomineralization, Hanover, NH Invited Lecture, "Using Silicatein Proteins and Biomimetic Molecules to Direct the Polycondensation of Organosilane and Organometallic Precursors", by J. Sumerel and D.E. Morse; presented by Jan Sumerel. 8/02

Workshop on Protein-Inorganic Interfaces, University of Washington, Friday Harbor Laboratory, Friday Harbor, WA

Invited Poster Presentation, "Catalysis of Synthesis and Structure-Directed Growth of Nanocrystalline Metal Oxides Using Proteins from Sponge Biosilica", by D. Kisailus, J. Sumerel, W. Yang, J. Weaver and D.E. Morse; presented by David Kisailus 10/02

Max Planck Institute-UCSB Workshop on Advanced materials, Mainz, Germany Poster Presentation, "Molecular Mechanisms Controlling Biosilicification in Marine Sponges, and Applications to Synthesis of Advanced Materials," by J. Weaver, J. Sumerel, D. Kisailus and D. Morse; presented by James Weaver. **Winner of first-place award for best poster presentation at the State-wide California Sea Grant Graduate Student Trainee Competition.** 11/02

California Sea Grant Graduate Student Trainee's Research Meeting, La Jolla, CA

## DISSERTATIONS

Michael T. Janicke (Chemical Engineering). "Probing Molecularly Engineered Inorganic-Organic Interfaces using Solid-State NMR". March, 1997.

Deron A. Walters (Physics). "Advanced Atomic Force Microscopy: Development and Application". June, 1997.

Christina DeLaRocha (EEMB). "Measurement of Silicon Isotope Ratio Variations in Dissolved Silicon and in Biogenic Silica: Demonstration of Isotopic Fractionation by Marine Diatoms During Opal Formation and Utility " December, 1997.

Ali Firouzi (Chemical Engineering). "Phase Behavior and Oriented Ordering in Silicate-Surfactant Liquid Crystals". June, 1997.

Angela M. Belcher.(Chemistry)"Proteins Controlling CaCO<sub>3</sub> Nucleation, Phase, and Orientation in Biocomposite Materials" January, 1998.

Angela M. Belcher.(Chemistry). "Spatial and Temporal Resolution of Interfaces, Phase Transitions and Proteins in Calcium Carbonate-Based Biocomposite Materials". January, 1998.

Charlotte Zaremba (Chemistry). "Structure and Reaction Studies of Biological Organic and Inorganic Composite Materials: Seashells, Diatoms, and a Unique Birch Bark". October, 1998.

Mark S. Morey, "Isomorphic Incorporation of d(0) Transition Metals into Mesoporous Silica", 1998

Tilman E. Schäffer (Physics). "Physical Methods in Nanoscale Science with the Atomic Force Microscope". March, 1998.

Christopher T. Brown (Materials). "Habit and Polymorph Modifications of Calcium Carbonate by Experimental Control". October, 1998.

Charlotte Zaremba (Chemistry). "Structure and Reaction Studies of Biological Organic and Inorganic Composite Materials: Seashells, Diatoms, and a Unique Birch Bark". October, 1998.

Mark S. Morey, "Isomoprphic Incorporation of d(O) Transition Metals into Mesoporous Silica", 1998

Dan Favre (Chemical Engineering) "Solid-state NMR Studies of Dynamics of Organic Molecules Adsorbed in Zeolites", 1998.

Vesna Saraba, M.S. (Chemistry) " Synthesis and Solid-State Characterization of Mesoporous MCM-48: A Kinetic Study & Post-synthesis Surface Modification of MCM-48" March 1999

Jennifer Cha (Chemistry). "Molecular Mechanisms of Biological Synthesis of Silica". September, 2000.

Mario Viani (Physics). "Improved Atomic Force Microscopy for probing Single Biomolecules", December 2000.

Jennifer Cha (Chemistry). "Learning from Nature: Novel Routes to Biomimetic Synthesis of Silica-Based Materials" September, 2000.

Scott Curtin, PhD (Chemistry) "Initiators for Chain-end functionalized polypeptides", 2001.

Jungyeon Hwang, PhD, (Chemistry) "Properties of biomimetic polypeptide materials: biomimetic adhesives and ethylene glycol functionalized beta-sheet forming polypeptides", 2002.

James Thompson (Physics). "Tools for Studying Biomaterials", March 2002.

YongJin Han, Ph.D. (Chemistry) (jointly supervised with A. Butler) "Synthesis and Inclusion Chemistry of Mesoporous Silicate SBA-15 and Related Materials" Spring 2002

## VISITS TO ARL AND OTHER DOD RESEARCH CENTERS

The frequency of these visits and their impact on research in our MURI program have both increased significantly over the past year:

1998:

Daniel Morse visit to U.S. Army Research Laboratory Research and Development Center (Natick, MA). Seminar and research discussions with Dr. Stephen Fossey (biomolecular polymers, high tensile strength fibers & elastomers, analysis & control of polymer interphases in fibers & films), Dr. John Walker (detox. enzymes, sensors, personnel-protecting fibers & filtrants), Dr. Heidi Gibson (transformation routes from siloxanes to silicon nitrides) and others. December, '97.

Brad Chmelka visit to U.S. Army Research Laboratory, Aberdeen Proving Ground and Edgewood Research, Development and Engineering Center (Aberdeen, MD). Seminar and research discussions with Dr. Richard Shuford (Chief, Polymers Research Branch), Dr. Nora Beck Tan (block copolymers), Dr. Ernest Chin (metals, ceramics, intermetallics, armor) and Dr. Erica Valdes (mesoporous filtrants for detox.), September, '98.

1999:

Daniel Morse participated in the Pentagon Briefing Series on Emerging Technologies, organized by the Deputy Undersecretary for Defense for Science and Technology. Presented briefing on the UCSB-ARO MURI project, and participated in four-services round-table discussion lead by Dr. Trew. Washington, D.C., January, '99.

Brad Chmelka visit to Wright-Paterson Air Force Base. Host, Dr. Thomas Cooper, member of the UCSB-MURI Advisory Panel. February, '99.

Galen Stucky participated in DARPA-Defense Science Research Council Meeting for the Study of Nanomaterials and Technologies, Arlington, VA, March, '99. Workshop focused on the fact that many technologies important to DoD rely on materials with unique properties dependent on features 5-50 nm in size. These materials are distinguished by methods of their synthesis, since dimensions are too small to be prepared by lithographic processing, yet too large to be prepared by conventional synthetic chemistry. This study addressed properties and opportunities in several material classes, with emphasis on examples from synthetic and polymer chemistry and biology.

Galen Stucky and Daniel Morse visit to U.S. Army Research Laboratory Research and Development Center (Natick, MA) for participation in Ballistics Protection Workshop, April, '99.

Daniel Morse visit to Naval Research Laboratory, Washington, D.C., May, '99. Host, Dr. Joel Schnur, Director, Biomolecular Materials Division. Presented seminar on "Biomolecular and Biomimetic Nanofabrication with Calcium, Transition Metals, Rare Earths and Silicon" in UCSB activity; conferred with NRL scientists on problems of mutual interest, including sensors, high-strength composites, and low-signature composites.

Galen Stucky visit to ARL/Aberdeen Proving Ground to participate in Workshop on "Templated Nanoscale Synthesis and Reactivity: Opportunities, Requirements, and Challenges," Goals were to identify opportunities in templated nanoscale synthesis and reactivity that can be utilized by the Department of Defense, and to define opportunities and challenges for utilization, October, '99.

2000:

Professor Chmelka is a member of the DARPA-financed Defense Sciences Study Group administered by the Institute for Defense Analyses in Washington, D.C. in conjunction with the Department of Defense. This intensive panel meets 3 weeks during each of two years and has over the past year involved the following field visits:

Air Force and Aerospace Facilities. Visits to TRW, Boeing, Lockheed-Martin, Nellis AFB, U.S. Space Command, U.S. Strategic Command, Whiteman AFB, Air Force Research Laboratory, Wright-Patterson AFB, June 19-26, 2000.

Nicholas Melosh was selected for a Graduate Student Award at the Spring, 2000 meeting of the Materials Research Society meeting.

Army, Navy, Marine, Coast Guard Facilities. Visits to U.S. Joint Forces Command, Atlantic Fleet (Norfolk), Camp LeJeune, U.S. Army Armor Center (Fort Knox), U.S. Coast Guard (Key West), U.S. Southern Command, U.S. Central Command, Kings Bay Submarine Base. August-14-22, 2000.

Intelligence agencies. Visits to National Reconnaissance Office, National Security Agency, Central Intelligence Agency Oct. 16-18, 2000.

2001:

Institute for Defense Analyses and U.S. Capitol. Meetings with U.S. Congressional representatives and committees associated with the armed services and science/technology. Feb. 12-14, 2001.



## LEVERAGED FUNDING FROM CORPORATIONS, FOUNDATIONS, ETC.

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#### (Cumulative)

Other Support Synergistic with this Award:

\$3,390,000	Morse, Deming, Hansma, Stucky	NASA/URETI	08/19/02 – 8/18/07
\$375,000	Morse	NASA	01-02
\$349,716	Morse	U.S. Department of Commerce NOAA Sea Grant Program	01-02
\$270,000	Morse	Army Research Office	01-02
\$70,000	Morse	Dow Corning Corporation	01-02
\$360,000	Morse, Stucky	NSF "Creativity Extension Award" (DMR-9634396)	01-02
\$411,000	Morse, Stucky	UC Systemwide BREPGGrant	01-02
\$105,000	Morse, Stucky, UCSB Addadi, Weiner, Weizmann Inst.)	Bi-national Science Foundation (U.S.-Israel)	01-02
\$83,000	Plaxco, Morse	Office of Naval Research	01-02
\$30,000,000	Princeton, UCSB, Northwestern , UNC, NASA-Langley – Plaxco, Morse	NASA	02-03
\$6,000,000	Morse	NASA UCSB Component of NASA-URETI	02-03
\$375,000	Morse	NASA (NAG1-01-003)	02-03
\$725,059	Morse	US Dept. of Energy	02-03
\$349,716	Morse	U.S. Department of Commerce NOAA Sea Grant	02-03
\$270,000	Morse	ARO	02-03
\$90,000	Morse	DOE – Oak Ridge	02-03
\$1,200,000	Morse	WM Keck Foundation	02-03

\$1,084,650	Hansma P., Hansma H, NIH Morse		05/02/02 – 04/30/06
\$225,000	Deming	NSF CHE-0099334	5/01/01 - 4/30/04
\$125,000	Morse	National Aeronautics and Space Administration	10/01/01 - 9/30/02
\$90,000	Morse	US Dept of the Army	9/29/01 - 9/28/02
\$90,000	Morse	Genencor Inc.	10/01/01 - 9/30/02
\$116,572	Morse	US Dept. of Commerce – Sea Grant	3/01/01 - 2/28/02
\$400,000	Hansma	NSF (Div.Matl. Res.)	7/01/00 - 6/30/03
\$60,000	Deming	Camille Dreyfus Teach.-Sch.	7/01/00 (5 yrs.)
\$50,000/yr	Deming	NSF/chem.&Transp.Syst.	2/15/00 - 1/31/02
\$27,937	Stucky	Dow Corning Corp.	1999-2000
\$26,000	Stucky/Chmelka	Daikin Ind.	1999-2000
\$347,322	Morse	Dept. of Comm.	3/01/98 - 2/28/01
\$560,000	Chmelka, Pine, Stucky	NSF (Div. Eng.)	9/01/98 - 8/31/00
\$800,000	Morse, Stucky, Hansma, Chmelka, Brzezinski, Deming, Hildebrand-UCSD	Dow Corning Corp.	1/01/98 - 12/31/01
\$18,000	Chmelka	NSF, Div. Itn'l Prog., (joint w/French CNRS & Univ. Paris, Jussieu)	4/01/98 - 3/31/00
\$48,000	Morse	Los Alamos Nat'l Lab- UC Collab.	11/01/98-10/31/99
\$45,000	Stucky	Triton Systems Inc.	1998-2000
\$ 65,000	Stucky, Morse	DuPont Corporation	1/01/97 - 2/31/97
\$200,000	Chmelka	David & Lucile Packard Foundation	(FY '97, '98 allocns)
\$150,000	Chmelka	NSF Young Investigator Award	(FY '97, '98 allocns)
\$20,000	Chmelka	Camille & Henry Dreyfus Teacher-Scholar Award	(FY '97, '98 allocns)
\$20,000	Chmelka	Alfred P. Sloan Foundation	(FY '97, '98 allocns)
\$25,000	Chmelka	Shell Research B.V., The Netherlands	(FY '97 allocn)
\$30,000	Chmelka	Los Alamos Nat'l. Lab- UC Collab.	(FY '97, '98 allocns)
\$20,000	Deming	ACS Petroleum Research Fund Startup Grant	(FY '97)

\$45,000	Stucky	Air Products and Chemicals, Inc.	1997
\$30,000	Stucky	Mobil Technology Company	1997-2000
\$350,000	Deming	NSF Career Award	5/01/97 - 4/30/01
\$210,000	Morse, Stucky (with Weiner & Addadi In Israel)	Binational Science Foundation (U.S.-Israel)	10/01/96 - 9/30/02
\$250,000	Morse, Stucky, Hansma, Chmelka Brzezinski, Deming	UCSB Admin., Col. of Engineering, Col. of L&S, Grad. Div. (Student Support)	10/01/96 - 9/30/02
\$700,000	Hansma	NSF (Div. Mat. Res.)	10/01/96 - 9/30/99
\$600,000	Morse, Stucky, Hansma, Chmelka, Deming	NSF (MRSEC); (via UCSB's MRL) (with DuPont)	10/01/96 - 9/30/01
\$947,102	Stucky, Morse	NSF (GOALI)	7/01/96 - 7/31/03
\$1,249,232	Morse, Stucky, Hansma	ONR	5/01/96 - 3/31/00
\$ 157,500	Morse, Stucky, Chmelka, Brzezinski Hansma,	Univ. of Calif. Biotechnology Training Grant (Student & P.Doc Supt.)	10/01/96 - 9/30/98
\$359,587	Morse, Hansma, Stucky	Dept. of Comm.	10/01/96 - 9/30/98
\$170,000	Hansma	Digital Instruments Inc.	1994-1999
<b>\$54,135,393</b>	<b>TOTAL</b>		

## TECHNOLOGY TRANSFER

1. Inventions/patents applications: See page 40

2. Industrial Interactions: Strong reciprocal interactions between our program and several potential beneficiary industries help guide and accelerate our research. In addition to direct matching financial support from several of these companies, we and our technology transfer partners benefit from frequent reciprocal research visits between MURI-supported faculty, postdoctoral and students and industrial researchers and research administrators of:

Dow Corning Corporation  
Dow Corning Chemical Company  
Battelle Pacific Northwest  
Amgen, Inc.  
Daiken U.S. Corporation  
CNRS-Rhodia  
Nusil, Technology, Inc.  
Raychem  
Triton Systems Inc.  
Genencor  
Semiconductor Research Corp.  
Shell

3. Army Research Laboratory Visits: See page 70

4. National Laboratories: Two Joint Projects have been initiated between our MURI -supported program and two teams of investigators at the Los Alamos National Laboratory. These are focused on (a) electrical field control of nanophase assembly; and (b) organic-inorganic interfacial control of thin-film silicon-based materials.